Master's Thesis

INVESTIGATION ON THE SPATIAL AND TEMPORAL VARIATIONS OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN ULSAN

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Department of Urban and Environmental Engineering

(Environmental Science and Engineering)

Graduate School of UNIST

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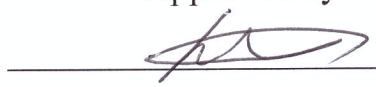

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Abstract

Large amounts of Volatile Organic Compounds (VOCs) are emitted from industrial facilities, and they can cause harmful effects to human health. Once emitted to the atmosphere, VOCs are dispersed into surrounding areas and directly inhaled by residents. Ulsan, known as the largest industrial city of South Korea, has many kinds of factories related to petrochemical, automobile, non-ferrous, and shipbuilding industries. Large VOC emissions are expected in Ulsan, thus continuous and intensive monitoring is required. The aim of this study is to investigate the levels, pattern, spatial distribution, main sources, and risk levels of VOCs in Ulsan, South Korea.

In this study, VOC monitoring in Ulsan was conducted using passive air sampler (Radiello 130 packed with 530 mg of active charcoal with particle size of 35−50 mesh). The samplers were deployed at 14 sites in Ulsan during summer (02-31 July (30 days) and 31 July-29 August, 2014 (30 days)), fall (08 October-07 November (30 days) and 07 November-05 December, 2014 (30 days)), winter (08 January-03 February (26 days) and 03 February-03 March, 2015 (30 days)), and spring (10 April-08 May (28 days) and 08 May-07 June, 2015 (30 days)). Sampling sites were divided into urban (U1-U8) and industrial (I1-I6) areas. The target compounds were 28 VOCs which were classified into three groups, including aromatic, halogenated, and others (alkene and oxygenated). Radiello cartridges were extracted, and the extracts were analyzed using a gas chromatograph/mass spectrometer (Agilent 7890A/5975C).

The target VOCs were generally detected at all sampling sites, indicating that VOCs are ubiquitous in Ulsan and not good for human health. Particularly, there were no significant differences in seasonal concentration of VOCs, because many industrial facilities, located in Ulsan, emit VOCs continuously regardless of weather. Among target groups, aromatic groups accounted for most of VOCs (66-86%), in detail, concentration of toluene was highest at all the sampling sites over the sampling periods. Also, most of total VOC concentrations were relatively high at industrial sites and low at urban sites. According to the spatial distributions of VOCs, all major industries of Ulsan seem to be the important VOC sources, especially automobile industrial complexes. To identify main sources of VOCs, a variety of statistical tools were used. As a result, non-traffic sources were dominant in Ulsan, and several compounds had a good correlation, indicating similar emission sources. Although there are many kinds of industrial facilities in Ulsan, risk was not serious according to risk assessment of benzene, toluene, ethylbenzene, and xylenes (BTEX). Through this preliminary study, we could identify seasonal major sources and risk levels of VOCs in Ulsan. This study is the first comprehensive study for VOCs including high resolution monitoring in Ulsan, therefore, it can be applied to other national industrial complexes in South Korea.

Contents

List of Figures

List of Tables

Ⅰ. INTRODUCTION

1.1 Volatile Organic Compounds (VOCs)

1.1.1 Definition and properties of VOCs

Volatile organic compounds (VOCs), known as hazardous air pollutants (HAPs), significantly affect air quality and human health (Valach et al., 2014). Generally, atmospheric VOCs react with nitrogen oxide (NO_X) emitted from any sources in the presence of sunlight, then ozone (O_3) and secondary organic aerosols (SOA) were produced (Figure 1) (Sarkar et al., 2014, Warneke et al., 2014, Yurdakul et al., 2013). These two compounds (O_3 and SOA) can adversely impact on crop yields, air quality, human health as well as contribute to the climate change (Pugliese et al., 2014, Villanueva et al., 2014). Also, oxidation of VOCs is possible at low vapor pressure and the compounds are vaporized well in the atmosphere (Huang et al., 2015, Yurdakul et al., 2013). Therefore, VOCs can be regarded as an important substance in the atmospheric environment.

Nowadays, periodic VOC monitoring is highly required to identify concentrations of common days because national institutes require management of responding system and an extent of damage prediction for chemical accidents. Actually, several VOCs were classified as accident preparation substances by the Korea Ministry of Environment (KME, 2014), and some compounds were classified into the carcinogenic compounds by International Agency for Research on Cancer (IARC, 2015).

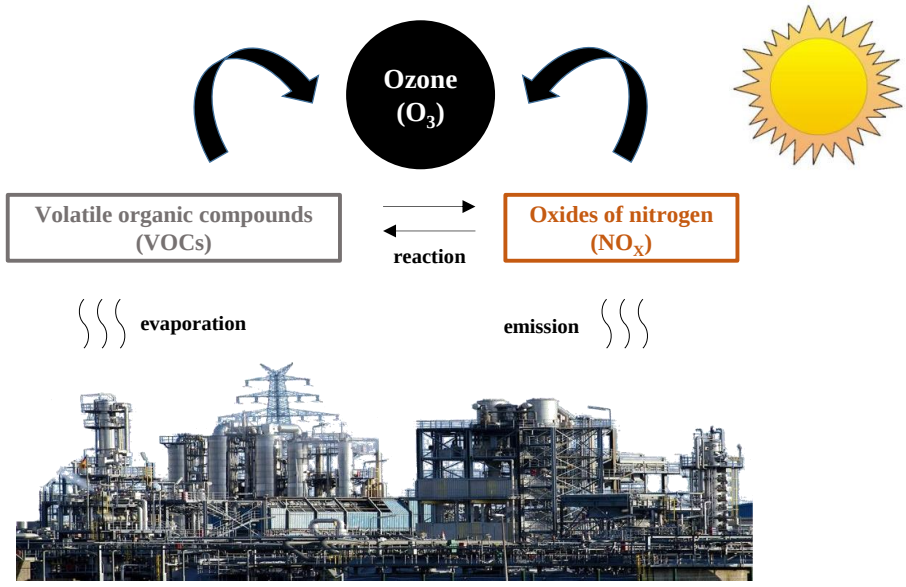

Figure 1. Procedure of ozone formation through VOCs and NO_X reaction in the atmosphere.

1.1.2 Toxicity of VOCs

Exposure to some VOCs can get a diversity of adverse health effects such as asthma, allergies, headaches, and chronic obstructive pulmonary disease (COPD) (Chen et al., 2015). Due to their severe influence to human body, many institutes all over the world are regulating and updating several VOCs according to characteristics of each compound.

VOCs have classified as carcinogenic or non-carcinogenic compounds by IARC, United States Environmental Protection Agency (US EPA), and American Conference of Governmental Industrial Hygienists (ACGIH). Classification of IARC has 5 groups including group 1 (carcinogenic to humans), 2A (probably carcinogenic to humans), 2B (possibly carcinogenic to humans), 3 (not classifiable as to its carcinogenicity to humans), and 4 (probably not carcinogenic to humans) (IARC, 2015). By 2005, US EPA classified VOCs into group A (carcinogenic to humans), B1 and 2 (likely to be carcinogenic to humans), C (suggestive evidence of carcinogenic potential), D (inadequate information to assess carcinogenic potential), and E (not likely to be carcinogenic to humans) (EPA, 2015). Furthermore, ACGIH also suggested the VOC carcinogen ability into group A1 (confirmed human carcinogen), A2 (suspected human carcinogen), A3 (confirmed animal carcinogen with unknown relevance to humans), A4 (not classifiable as a human carcinogen), and 5 (not suspected as a human carcinogen) (ACGIH, 2015).

The classification of VOC by three institute were presented in Table 1. Among the VOCs, 1,2-Dichloroethane (2B and B2), 1,3-Butadiene (1 and A), benzene (1 and A), and vinyl chloride (1 and A) are especially classified as carcinogenic compounds by IARC and US EPA (Boynard et al., 2014, Chen et al., 2016). Although concentration of toluene (3 and D), ethylbenzene (2B and D), xylene (3 and D) in the atmosphere are higher than other VOCs, these compounds are not classified as carcinogenic compounds by IARC and US EPA (Chen et al., 2015). Thus, VOCs need to be evaluated to identify chemical properties and risk on human health.

Table 1. Toxicity of major VOCs suggested by EPA, IARC, and ACGIH.

Compounds	EPA 1986	EPA 1999	EPA 2005	IARC	ACGIH
1,1,1-Trichloroethane	-	-	D	3	A4
1,1,2-Trichloroethane	C	-	-	3	A3
1,1-Dichloroethylene	C	-	-	3	A4
1,2,4-Trichlorobenzene	D	-	-	-	-
1,2-Dichlorobenzene	D	-	-	3	-
1,2-Dichloroethane	B2	-	-	2B	A4
1,2-Dichloropropane	-	-	-	1	A4
1,3-Butadiene	-	A	-	1	A2
1,4-Dichlorobenzene	-	-	-	2B	A3
Benzene	A	-	-	1	A1
Bromodichloromethane	B2	-	-	2B	-
Bromoform	-	-	-	3	A3
Carbon Tetrachloride	B2	-	-	2B	A2
Chlorobenzene	D	-	-	-	A3
Chloroform	B2	-	-	2B	A1
cis-1,2-Dichloroethylene	-	-	D	-	-
Dibromochloromethane	C	-	-	3	-
Dichloromethane	-	-	B1	2A	A3
Ethylbenzene	D	-	-	2B	A3
m,p-Xylene	-	D	-	3	A4
MTBE	-	-	-	3	A3
o-Xylene	-	D	-	3	A4
Styrene	-	-	-	2B	A4
Tetrachloroethylene	-	-	B	2A	A3
Toluene	-	-	D	3	A4
trans-1,2-Dichloroethylene	-	-	D	-	-
Trichloroethylene	-	-	A	1	A2
Vinyl chloride	A	-	-	1	A1

1.1.3 Sources of VOCs

VOC sources can be divided into two types including natural sources from shrubs and grasslands, and anthropogenic sources from industrial facilities and automobiles (Bhattacharya et al., 2015, Tassi et al., 2013). However, emission amount from the anthropogenic sources is larger than that of from natural sources. Therefore, monitoring and management of anthropogenic sources for VOCs are required.

There are many kinds of anthropogenic sources for VOCs from petroleum refining, painting, fossil fuels, solvent usage, and other industrial processes (Figure 2) (Ly-Verdu et al., 2010). In urban areas, main sources of VOCs are motor vehicle exhausts and evaporative emissions (Maisey et al., 2013, Wang and Zhao, 2008). For example, if VOC monitoring results show that concentration at a street or center of the city is the highest values, traffic sources are main source of VOCs in the study areas. Thus, VOC emissions of automobile, motorcycle, and any other vehicle should be regulated according to any standard levels. Moreover, if VOCs emitted nearby industrial complexes is detected at a very high level, it will be due to some industrial processes.

Figure 2. A variety of VOC sources from anthropogenic and natural environment.

1.2 Passive air samplers

There are some kinds of active and passive air samplers for VOC monitoring such as canister, tenax-tube, tedlar bag, Radiello, and 3M OVM (Figure 3). In previous studies, they can collect air samples using active air samplers quickly and interpret variation of VOCs by time scale (FLOCAS et al., 2003, Jian et al., 2015, Rella et al., 2014). However, active air samplers have some disadvantages such as weight, cost, and electricity requirement, and difficulty in supporting a high resolution spatial distribution of pollutant.

On the other hand, passive air samplers have lower cost and easier operation than active air samplers (Bruno et al., 2008, Gallego et al., 2011). Thus, it is possible to represent spatial distribution and identify hot spot of VOCs with high resolution (Choi et al., 2012). In addition, It is difficult to determine the hot spots of anthropogenic emission sources by using active air samplers because of short deployed time, while passive air samplers can help to obtain the VOC average concentrations owing to long sampling period such as 1 week or 30 days (Kouniali et al., 2003). However, passive air sampler which based on average concentration cannot catch some big events such as hazardous chemical accidents or traffic congestions.

Previous studies conducted researches about comparison between active and passive air samplers, and the results showed that there were no significant differences in the concentrations between two sampling approaches (Gallego et al., 2011).

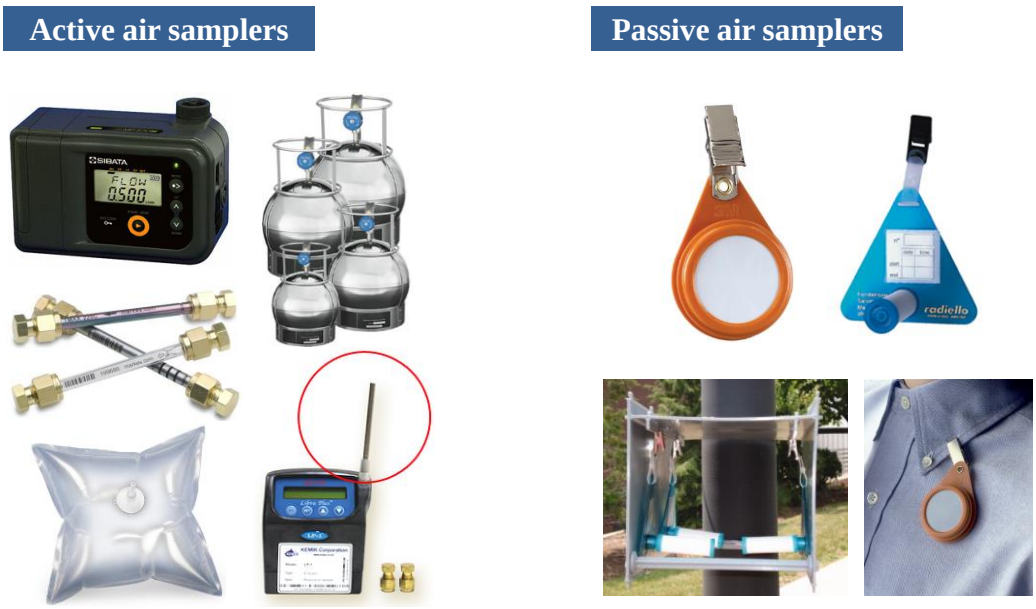

Figure 3. The kinds of active (tenax-tube, canister, and tedlar bag) and passive air samplers (Radiello and 3M OVM) typically used in previous studies.

There are some kinds of passive samplers for atmospheric VOCs, among them, 3M Organic Vapor Monitors (OVM) and Radiello were used frequently (Table 2). According to literature review, most of previous studies typically used the Radiello more than 3M OVM. Previous studies, which conducted in Turkey, Spain, Canada, and so on, suggested that concentration of some VOCs from multi-seasons, years, and sites could be identified by using passive air samplers (Dumanoglu et al., 2014, Miller et al., 2012, Parra et al., 2006, Zhang et al., 2014). There are several studies for indoor VOCs. Actually, previous studies in Mexico City (Ortiza et al., 2002), Peru (Han et al., 2005), US (Riediker et al., 2003), India (Mukherjee et al., 2003), Korea (Kim et al., 2001), and China (Lau and Chan, 2003) reported that workers, commuters who work indoor can expose to higher VOC concentration because people spend over 70% of their time at home or work place. In addition, other researches also studied on the influence of environmental conditions and determination of modelled sampling rates (Pennequincardinal et al., 2005), comparison of Radiello, 3M OVM, and Lanwatsu (Lan and Binh, 2012), and the impact of reduction in the benzene limit value (Simon et al., 2004). Radiello can be used under deteriorating weather including raining, snowing, and typhoon.

Furthermore, it detects low concentration and has high adsorbing abilities that accept sampling periods (15 minutes-30 days) and concentration range (1 ppb-1000 ppm) (SIGMA-ALDAICH, 2015). Consequently, Radiello passive air samplers were used in order to investigate the spatial and temporal distribution of VOCs.

Table 2. Trend of researches for passive air samplers (kinds of sampler, target VOCs, locations, periods, and analytical instruments).

Samplers	Target VOCs	Locations	Periods	Analytical instruments	Literatures
Radiello	20 VOCs	both	2 weeks	TD-GC/MS	(Gallego et al., 2011)
Radiello	23 VOCs	both	1 week	GC/FID	(Geiss et al., 2011)
Radiello	Benzene	outdoor	2 weeks	TD-GC/MS	(Plaisance et al., 2008)
Radiello	3 VOCs	outdoor	5 days	GC/FID	(Morales Terres et al., 2010)
Radiello	Benzene	both	1 week	GC/FID	(Kouniali et al., 2003)
Radiello	3 VOCs	indoor	1 day	TD-GC/MS	(Krol et al., 2014)
Radiello	BTEX	outdoor	1 day	GC/FID	(Lan and Binh, 2012)
Radiello	40 VOCs	indoor	8 days	TD/GC/MS	(Maisey et al., 2013)
Radiello	21 VOCs	outdoor	1 week	TD-GC/MS	(Bruno et al., 2008)
Radiello	140 VOCs	outdoor	2 weeks	TD-GC/MS	(Parra et al., 2006)
Radiello	BTEX	indoor	1 week	TD/GC/MS	(Rella et al., 2014)
Radiello	174 VOCs	outdoor	1 week	TD-GC/MS	(Roukos et al., 2009)
Radiello	26 VOCs	outdoor	2 days	HS-GC/MS	(Ly-Verdu et al., 2010)
Radiello	BTX	outdoor	3 weeks	GC/MS	(Simon et al., 2004)
Radiello	BTEX	outdoor	1 week	GC/FID	(Kerchich and Kerbachi, 2012)
Radiello	58 VOCs	outdoor	1 week	GC/MS	(Dumanoglu et al., 2014)
3M OVM	9 VOCs	both	4 weeks	GC/FID	(Begerow et al., 1995)
3M OVM	BTEX	both	1 day	GC/MS	(Demirel et al., 2014)
3M OVM	30 VOCs	both	2 days	GC/MS	(Tovalin-Ahumada and Whitehead, 2007)
3M OVM	8 VOCs	both	4 weeks	GC/FID	(Begerow et al., 1999)
3M OVM	29 VOCs	outdoor	3 days	GC/MS	(Chung et al., 2009)
3M OVM	23 VOCs	indoor	a month	GC/FID	(Colman Lerner et al., 2012)
3M OVM	BTEX	outdoor	2 weeks	GC/MS	(Miller et al., 2012)
3M OVM	BTEX	both	1 week	GC/FID	(Schneider et al., 2001)

1.3 Ulsan city, South Korea

1.3.1 Information of Ulsan

There are many national industrial complexes locating in Ulsan, Sihwa and Banwol, Yeosu and Gwangyang, Busan, Pohang, Daesan, Gumi and Daegu, and Geoje in South Korea. Among them, Ulsan city has the biggest heavy industrial complexes which including petrochemical, automobile, non-ferrous, and shipbuilding industries (Choi et al., 2012, KIM et al., 1998, Kwon and Choi, 2014, Park et al., 2008). Therefore, emission amount of chemicals in Ulsan remained the third position in Korea as mentioned by Pollutant Release and Transfer Registers (PRTR) data of the Ministry of Environment (Figure 4) (PRTR, 2015). Location area of Ulsan (1,057 km^2) is smaller than those of Kyounggi (10,171 km^2) and Kyoungnam (10,522 km^2) but the chemical emission amount in Ulsan is larger than both cities. Consequently, the emission density in Ulsan was the largest in South Korea.

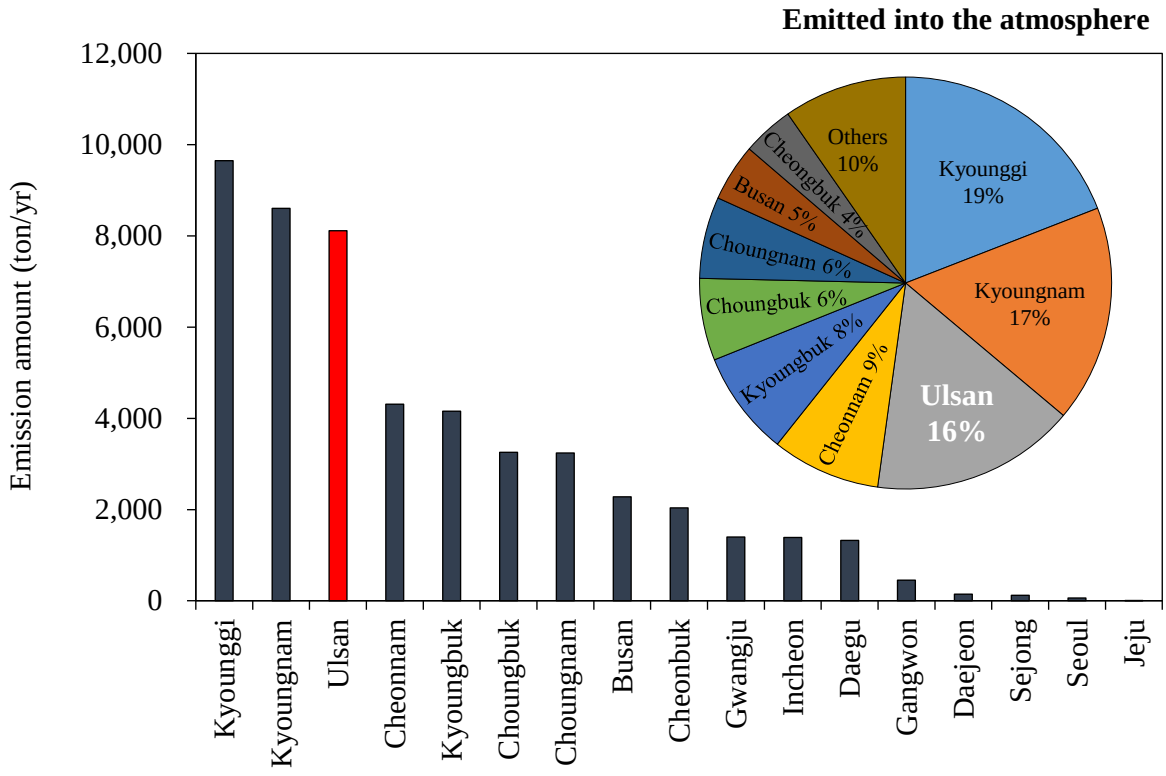

Figure 4. Emission amounts of hazardous chemicals emitted into the atmosphere reporting from PRTR in South Korea.

In addition, according to emission amounts of each compound as shown in Figure 5, only 18 chemicals were emitted upper 1% of the total chemicals. Among 131 chemicals emitted from 195 factories, xylene (m, p, o-xylene) had the highest concentration, followed by ethylbenzene and toluene. Especially, among BTEX, xylene, ethylbenzene, and toluene, known as main source of VOCs, account for most of chemicals.

Urban, residential, and commercial areas of Ulsan are nearby industrial complexes locating along the coast of east, so it is expected that people living in Ulsan can be exposed to a variety of VOC sources.

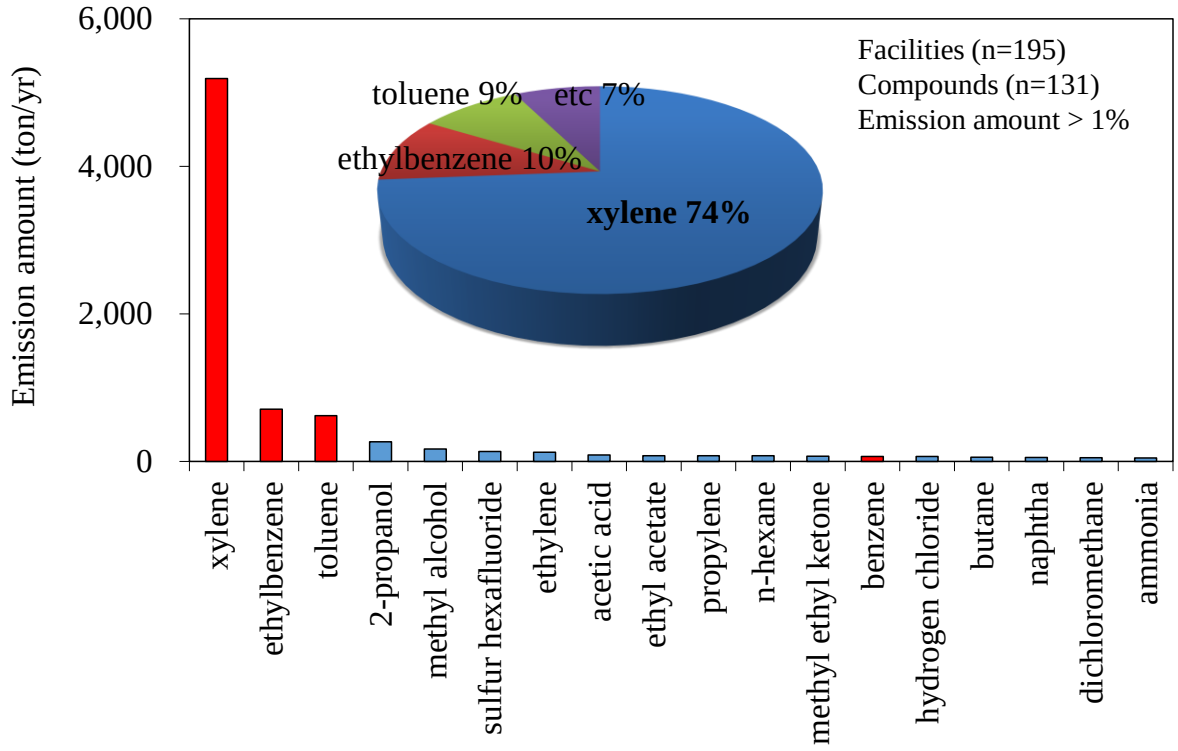

Figure 5. Emission amount of chemicals in Ulsan based on PRTR information system.

1.3.2 Previous studies about VOCs in Ulsan

Up to now, many kinds of studies about VOCs, especially source identification have been continuously conducted. Through the diagnostic ratios, correlation analysis, and principle component analysis, main sources of VOCs are identified as vehicle exhaust, industrial complexes, or natural effects. Also, a wide variety of researches focused on risk assessment which is mostly conducted about benzene, toluene, ethylbenzene, and xylenes. Among BTEX which mainly accounted for VOCs, benzene is mostly emitted by traffic sources in urban areas and classified as carcinogenic compounds by US EPA. Thus, researches on the monitoring of VOCs are constantly studying and interpreted through various tools and methods.

On the other hand, regarding both domestic and international studies, VOC monitoring in Ulsan has been reported to be extremely rare. Figure 6 shows all of the VOC previous studies. As can be seen from this figure, most of international articles focused on characteristics of particulate matter (Leea et al., 2004), atmospheric deposition (Lee and Lee, 2004) and load dust of PAHs (Dong and Lee, 2009, Lee and Dong, 2010), concentration (Susaya et al., 2013) and contribution of ozone (Lee et al., 2008, Lee et al., 2007), and children exposure to VOCs (Lee et al., 2002a). Only one of them conducted monitoring of VOCs using a canister as active air sampler. According to this article, VOCs were measured at two sites, one site at downtown area and the other at industrial area. As a result of comparison between two sites, concentration of VOCs at industrial sited were approximately four times higher than those at urban site. VOCs at downtown site mainly related to vehicle exhausts and evaporation emissions due to ethylene, propylene, acetylene, butanes, and pentanes. Those at industrial area were largely associated with petrochemical industries because of vinyl chloride, cyclohexane, and tetrahydrofuran. Also, the results of this research mentioned that industrial area could affect the urban area by transportation of ambient air (Na et al., 2001).

As a result of monitoring of VOCs in Ulsan, the concentrations were normally higher than those of other cities in the world, and almost studies were used active air samplers.

In domestic studies, they have studied about indoor air (Lee, 2011), comparison of indoor and outdoor air (Lim, 2011), exposure to a human health (Moon, 2015), and analytical methods for VOCs (Seo, 2002). Furthermore, they also focused on seasonal variation of 69 VOCs through five sampling sites, and source identification of VOCs by using correlation analysis and principle component analysis (Jung, 2010). As a result, vehicle exhaust, solvent usage, and oil refining at petrochemical complex were the highest VOC sources, followed by steel coating and smelt. There was a study on risk assessment. Four carcinogenic (1,3-butadiene, benzene, ethylbenzene, and trichloroethylene) and three non-carcinogenic

(o-xylene, styrene, and toluene) compounds were evaluated the risk level by using Monte Carlo simulation (Yoo, 2013). As a consequence of risk assessment, all of the non-carcinogenic compounds had risk lower value than 1.0 (limited value), 1,3-butadiene, benzene, and ethylbenzene had a cancer risk.

Thus, various domestic and international studies on monitoring and risk assessment of VOCs were performed by using several tools and Monte Carlo simulation, therefore, that is why researches on VOCs are required in Ulsan.

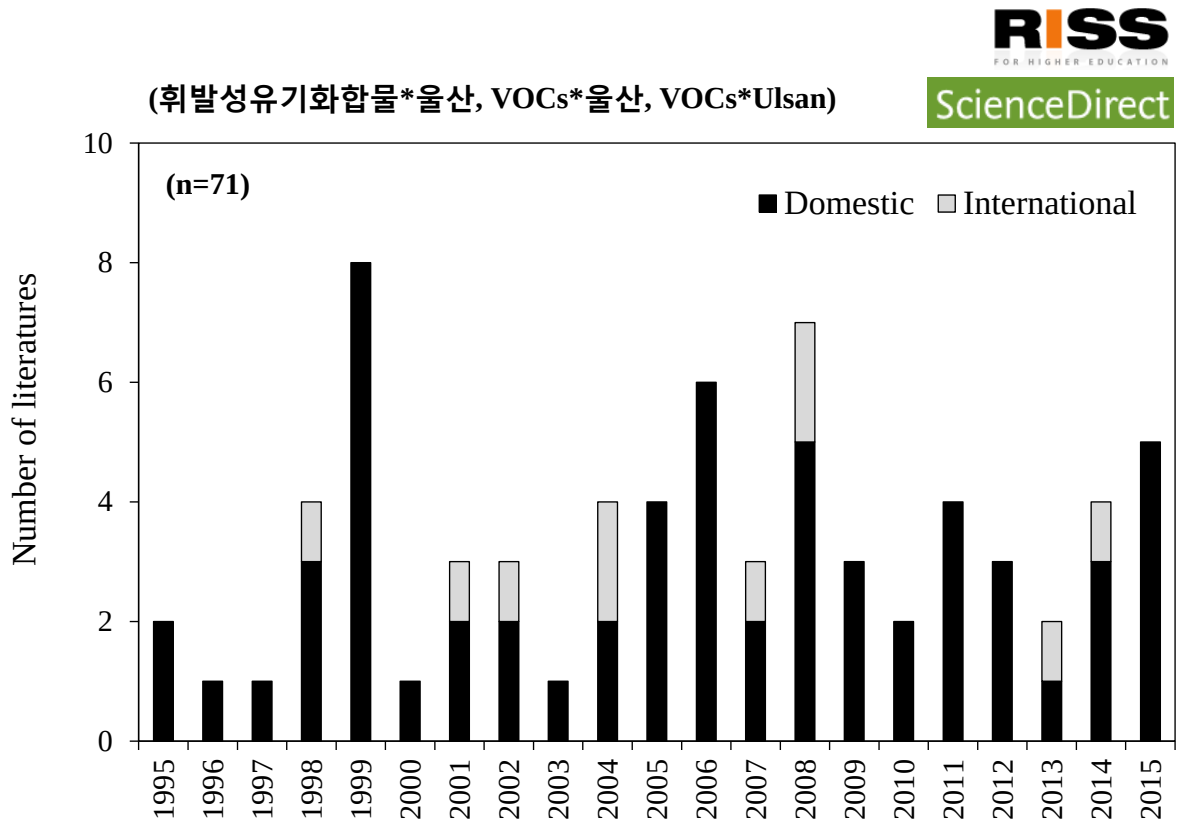

Figure 6. Domestic and international previous studies for atmospheric VOCs in Ulsan.

1.4 Objectives of this study

The overall purposes of this study are to investigate the concentrations, patterns, spatial and temporal distribution, source apportionment, and risk level of VOCs (Figure 7). This study conducted seasonal monitoring of VOCs in Ulsan. Passive air samplers were deployed at 14 sites (8 urban and 6 industrial sites). The detail objectives of this study are (1) to investigate not only levels and patterns of VOC but also criteria air pollutants and meteorological conditions at VOC sampling sites, (2) to determine spatial and temporal distribution of these pollutants, (3) to identify the main sources of VOCs in Ulsan such as petrochemical and automobile facilities, vehicle exhausts, fossil fuels, and so on, and (4) to assess the risk level of carcinogenic and non-carcinogenic VOCs via inhalation exposure to human in Ulsan.

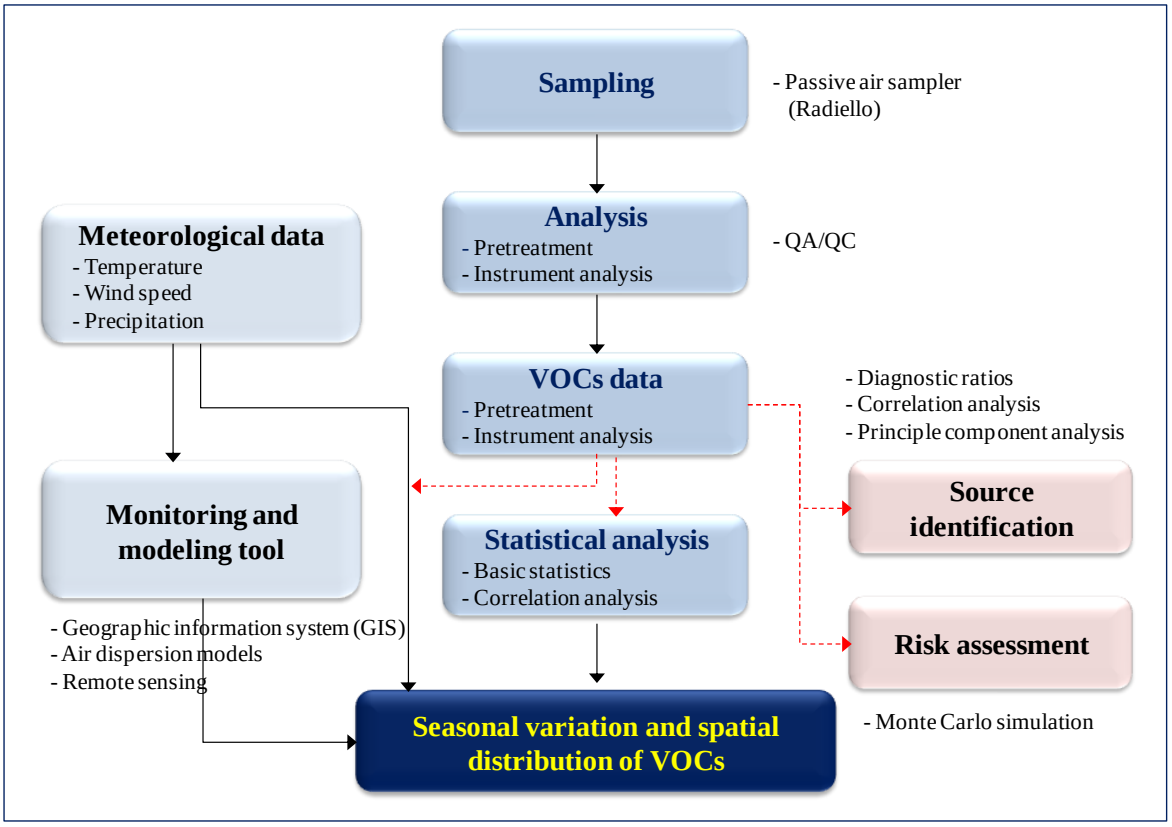

Figure 7. Overall schematic objective of this study.

Ⅱ. MATERIALS AND METHODS

2.1 VOC sampling

The study area is located at the south-eastern part of the Korean Peninsula (Figure 8). The samples were collected at 14 sites, which are classified into urban (U1-U8) and industrial (I1-I6) areas. Among these 14 sites, 11 sites are same with the sampling sites of Ulsan Institute of Health and Environment (UIHE), supported by the Korean Ministry of Environment, other 3 sites were selected in industrial sites (I5 and I6) and urban site (U2) in order to assess the spatial resolution of VOC. Site U2 was selected because it is located nearby automobile industrial complex but there are many people are living here.

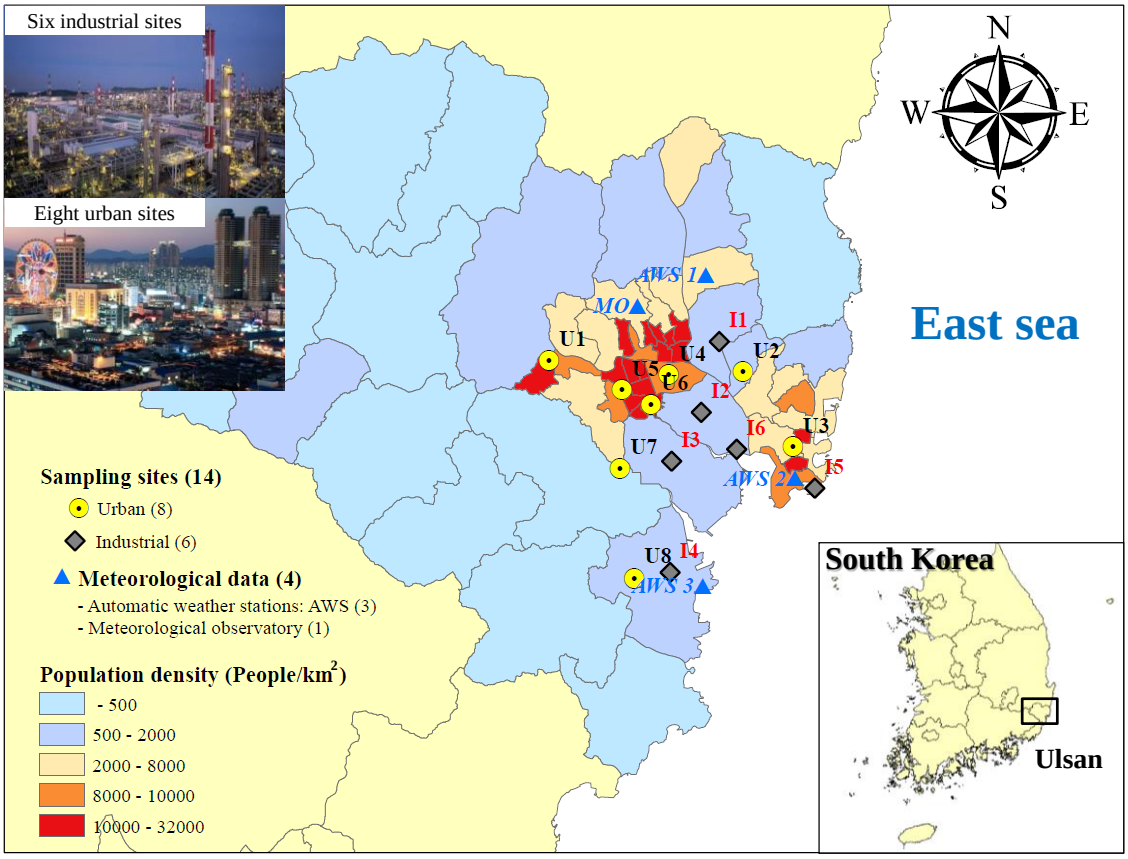

Figure 8. Study areas, divided by six industrial and eight urban sites, three automatic weather stations, and one meteorological observatory based on population density.

For VOC monitoring, Radiello® diffusive air sampler (Supelco, co.) was used as passive air sampler. The sampler consists of white diffusive body, triangular supporting plate, and adsorbing cartridge (Figure 9). The adsorbing cartridge consists of a stainless steel cylinder (100 mesh grid and 5.8 mm diameter), and activated charcoals (530±30 mg and 35-50 mesh) are packed inside. During VOC sampling, a cartridge were fixed in a white diffusive body, which is made of 1.7 mm microporous polyethylene thick, 25 μm porosity, and 18 mm diffusive pate length. This white diffusive body, fixed with cartridge, was placed onto the triangular supporting plat.

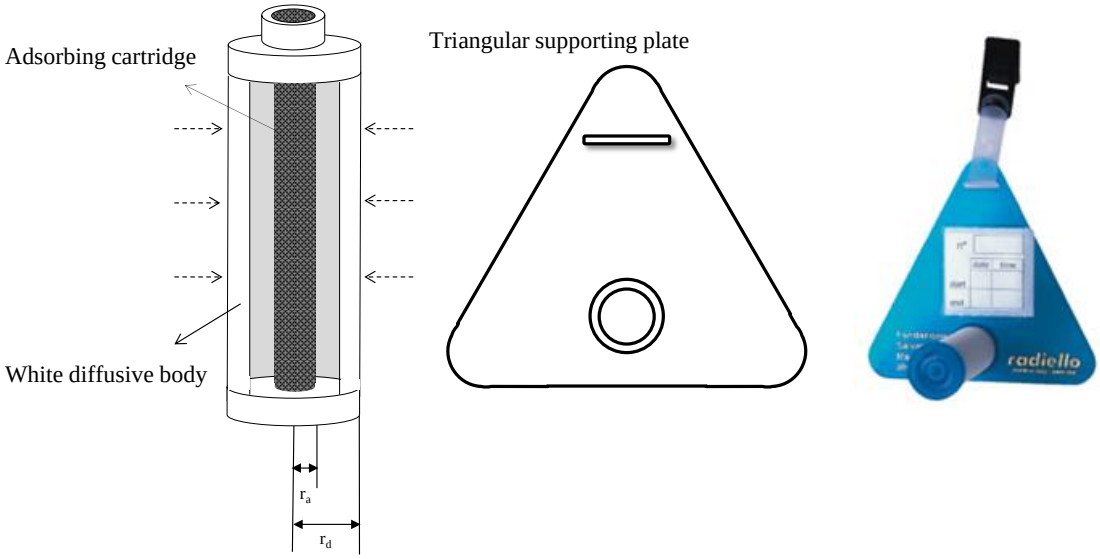

Figure 9. A drawing of passive air sampler (Radiello).

VOC sampling was conducted during four seasons (summer, fall, winter, and spring) at 14 sites in Ulsan (Figure 10). Each season consisted of two campaigns as follows: summer (02-31 July (30 days) and 31 July-29 August, 2014 (30 days)), fall (08 October-07 November (30 days) and 07 November-05 December, 2014 (30 days)), winter (08 January-03 February (26 days) and 03 February-03 March, 2015 (30 days)), and spring (10 April-08 May (28 days) and 08 May-07 June, 2015 (30 days)). Ultimately, twenty-eight Radiello samplers were deployed in duplicate at 14 sites. After sampling, the cartridges were stored in a glass container at -10℃ until analyzed.

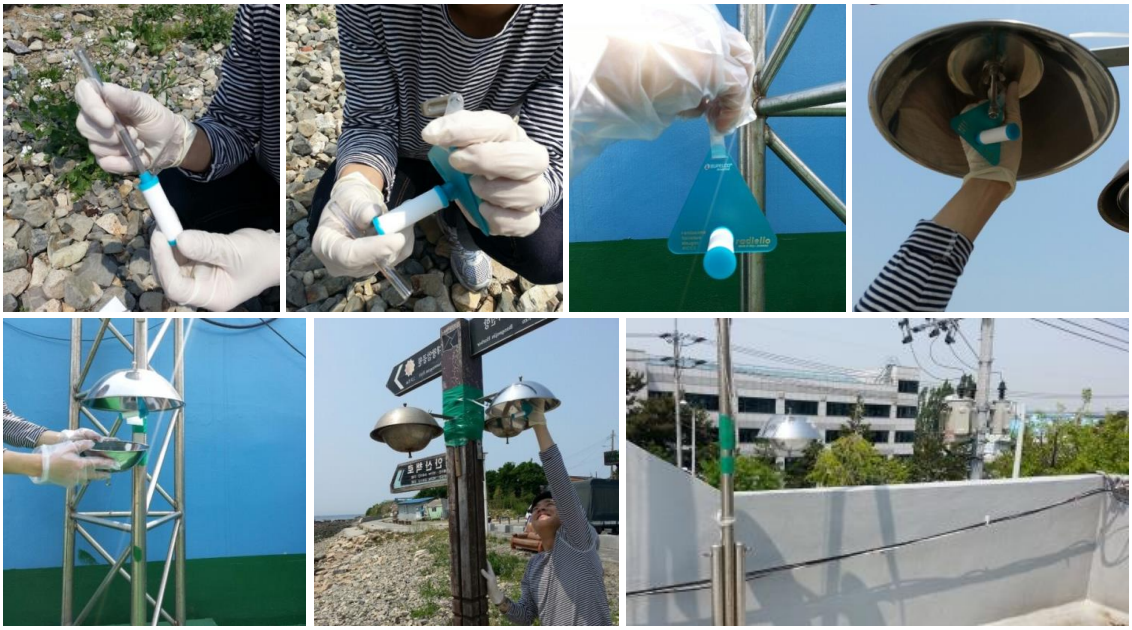

Figure 10. Images of VOC sampling at each site using passive air sampler.

2.2 Meteorological conditions and Criteria air pollutants (CAPs)

It is important to understand meteorological conditions and levels of criteria air pollutants during sampling periods, therefore, meteorological data such as wind speed and direction, temperature, precipitation, and humidity was obtained from the Korea Meteorological Administration (KMA) in this study (KMA, 2015). There are one meteorological observatory (MO) and nine automatic weather stations (AWS) in Ulsan, but only four automatic weather stations were selected. Also, information on criteria air pollutants were obtained from Ulsan Institute of Health & Environment (UIHE) (UIHE, 2015). According to data of UIHE, PM_{10}, SO_2, O_3, NO_2, CO were observed at 14 stations, and monitoring of VOCs have conducted at 2 stations (one urban and other industrial site) in Ulsan (KME, 2014-2015).

2.3 Analysis and QA/QC

The target compounds in this study were 28 VOC species: Benzene, Ethylbenzene, m,p-Xylene, o-Xylene, Styrene, Toluene, 1,1,1-Trichloroethane, 1,1,2-Trichloroethane, 1,1-Dichloroethylene, 1,2,4-Trichlorobenzene, 1,2-Dichlorobenzene, 1,2-Dichloroethane, 1,2-Dichloropropane, 1,4-Dichlorobenzene, Bromodichloromethane, Bromoform, Carbon tetrachloride, Chlorobenzene,

Chloroform, cis-1,2-Dichloroethylene, Dibromochloromethane, Dichloromethane, Tetrachloroethylene, trans-1,2-Dichloroethylene, Trichloroethylene, Vinyl chloride, 1,3-Butadiene, Methyl tert-butyl ether (MTBE). As can be seen from Table 3, target VOCs were divided into aromatic, halogenated, and other compounds (alkane and oxygenated) according to chemical characteristics of each compound.

Table 3. Information about groups and ions of target compounds, surrogate standards, and internal standard.

Groups	Target compounds	Target ions	Qualifier ions
Aromatic compounds	Benzene	78	77
	Ethylbenzene	91	106
	m,p-Xylene	91	106
	o-Xylene	91	106
	Styrene	104	103
	Toluene	91	92
Halogenated compounds	1,1,1-Trichloroethane	97	99
	1,1,2-Trichloroethane	97	83
	1,1-Dichloroethylene	61	96
	1,2,4-Trichlorobenzene	180	182
	1,2-Dichlorobenzene	146	148
	1,2-Dichloroethane	62	64
	1,2-Dichloropropane	63	62
	1,4-Dichlorobenzene	146	148
	Bromodichloromethane	83	85
	Bromoform	173	171
	Carbon tetrachloride	117	119
	Chlorobenzene	112	77
	Chloroform	83	85
	cis-1,2-Dichloroethylene	61	96
	Dibromochloromethane	129	127
	Dichloromethane	49	84
	Tetrachloroethylene	166	164
	trans-1,2-Dichloroethylene	61	96
	Trichloroethylene	130	132
	Vinyl chloride	27	62
Other compounds (Alkane and Oxygenated)	1,3-Butadiene	39	54
	MTBE	73	41
Surrogate standards	Methylene chloride-d_2	51	86
	1,2-Dichloroethane-d_4	65	67
	Benzene-d_6	84	56
	Toluene-d_8	98	100
	Chlorobenzene-d_5	117	82
	Ethylbenzene-d_{10}	97	116
	1,2-Dichlorobenzene-d_4	150	152
	1,4-Dichlorobenzene-d_4	150	152
Internal standard	Fluorobenzene	96	70

After sampling, the samples were proceeded according to the steps presented in Figure 11. Firstly, 2 mL carbon disulfide (CS_2) was added into the glass container with cartridge. As surrogate standards, deuterated VOCs (Methylene chloride-d_2, 1,2-Dichloroethane-d_4, Benzene-d_6, Toluene-d_8, Chlorobenzen-d_5, Ethylbenzene-d_{10}, 1,2-Dichlorobenzene-d_4, and 1,4-Dichlorobenzene-d_4) were also inserted into the cartridges before extraction. Using an ultrasonic bath, samples were extracted for 30 min and then 1 mL extracts were transferred to a vial. As an internal standard, fluorobenzene was added to the vial before injection at an analytical instrument.

After the pretreatment procedures, samples were analyzed by a Gas Chromatograph/Mass Spectrometer (GC/MS, Agilent 7890N/5975C) (Figure 12). A DB-624 column (60 m × 0.25 mm i.d., 1.4 µm film thickness) was used for separation of target compounds. The carrier gas was helium and operated at 1.00 mL/min. One µL of each sample was injected into GC in split mode (ratio is 25:1, 30 mL/min) and selective ion monitoring (SIM) mode. The oven temperature was as follows (Table 4): 40℃ initial for 3 min, increased at 8℃/min to hold at 90℃ for 4 min, and then increased at 6℃/min to a hold at 200℃ for 5 min. Ionization mode of the GC/MS was the electron ionization (EI). Finally, one of the chromatograms was shown in Figure 13.

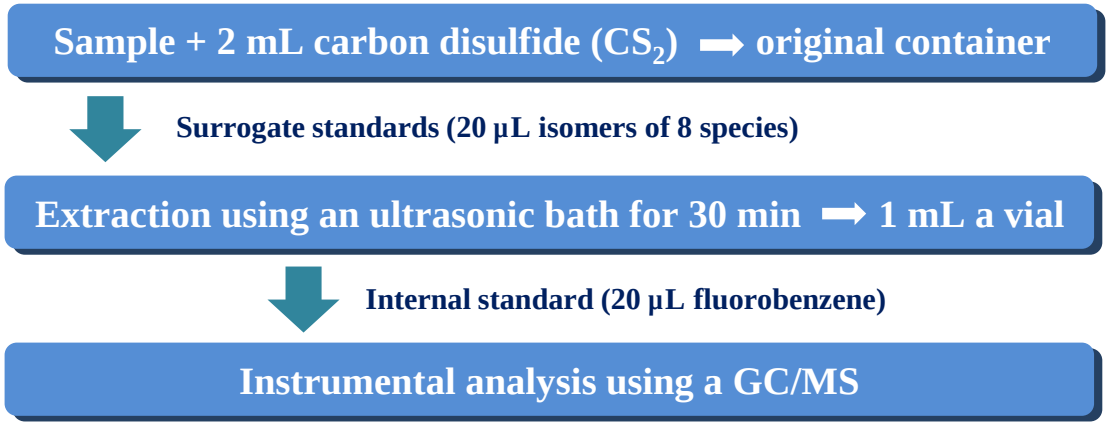

Figure 11. Scheme of the VOC analysis from pretreatment to instrumental analysis.

Table 4. Conditions of analytical instrument (GC/MS).

Items	Instrument conditions
Injection	235℃
Injection mode	Split 25:1, 30 mL/min
Carrier gas	Helium (99.999%), 1.00 mL/min
Column	DB-624 (60 m length, 0.25 mm inner diameter, and 1.4 μm thickness)
Oven condition	40°C (3 min)→8°C/min→90°C (4 min)→6°C/min→200°C (5 min)
Ionization voltage	70 eV
Mode	EI/SIM

Figure 12. Analytical instrument (GC/MS, Agilent 7890N/5975C).

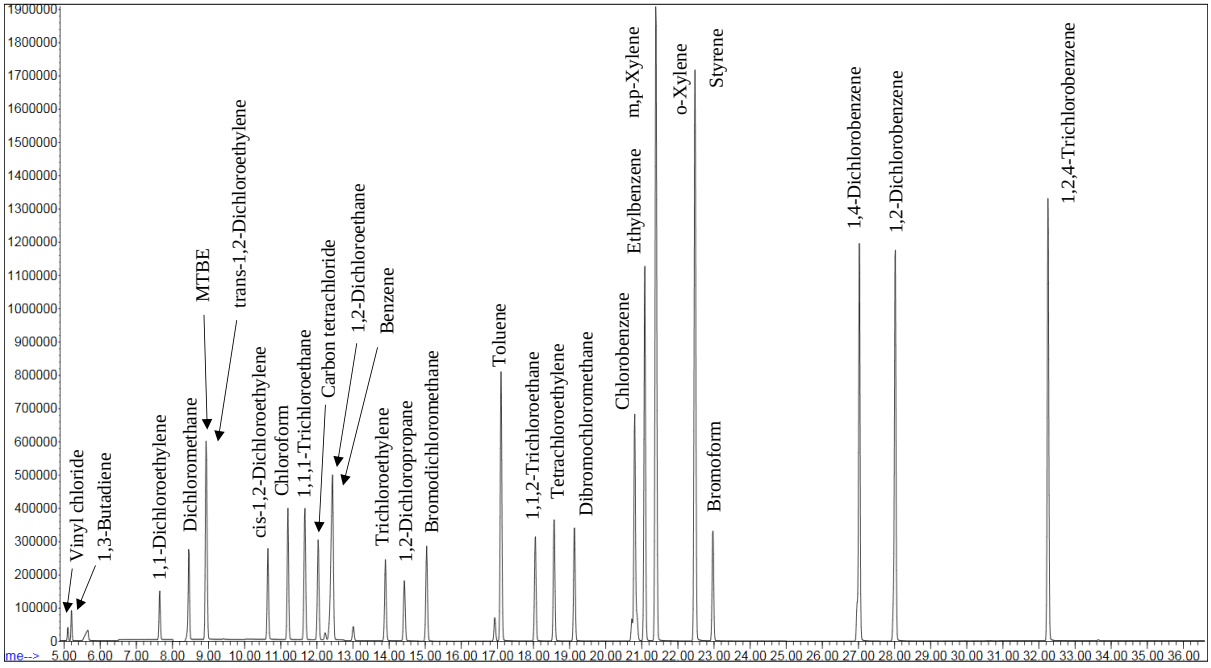

Figure 13. Chromatogram of target compounds (28 VOCs).

For quality control and quality assurance, field blanks, method detection limit (MDL), and instrumental detection limit (IDL) were used for accuracy of data. Every three field blanks were conducted in all of the seasons (n=24). Among 28 VOCs, only 18 VOCs were detected in field blanks, and average concentrations of field blanks were 0.028 μg/m^3, 0.002 μg/m^3, 0.002 μg/m^3, 0.009 μg/m^3, 0.001 μg/m^3, 0.010 μg/m^3, 0.001 μg/m^3, 0.003 μg/m^3, 0.002 μg/m^3, 0.002 μg/m^3, 0.003 μg/m^3, 0.002 μg/m^3, 0.001 μg/m^3, 0.008 μg/m^3, 0.009 μg/m^3, and 0.032 μg/m^3 for dichloromethane, chloroform, 1,2-dichloroethane, benzene, 1,2-dichloropropane, toluene, tetrachloroethylene, chlorobenzene, ethylbenzene, m,p-xylene, o-xylene, styrene, bromoform, 1,4-dichlorobenzene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene, respectively.

In case of MDL, seven samples spiked known concentration like calibration standard 1 (CS 1: 0.1 μg) were analyzed with an analytical procedure of real samples, and for IDL, CS 1 was analyzed using GC/MS for seven times. Finally, IDL and MDL were calculated using standard deviations which were obtained through seven replicates of IDL (Table 5) and MDL (Table 6).

Table 5. The results of instrumental detection limit (IDL) and limit of quantification (LOQ) for 28 VOCs.

($\mu g/m^3$)	IDL1	IDL2	IDL3	IDL4	IDL5	IDL6	IDL7	SD	IDL	LOQ
Vinyl chloride	0.038	0.036	0.036	0.038	0.038	0.037	0.039	0.001	0.003	0.034
1,3-Butadiene	0.024	0.022	0.021	0.026	0.022	0.026	0.022	0.002	0.006	0.061
1,1-Dichloroethylene	0.022	0.020	0.019	0.019	0.021	0.019	0.021	0.001	0.004	0.043
Dichloromethane	0.050	0.049	0.052	0.050	0.048	0.052	0.049	0.002	0.005	0.048
MTBE	0.033	0.036	0.038	0.033	0.033	0.039	0.038	0.003	0.009	0.090
trans-1,2-Dichloroethylene	0.036	0.036	0.033	0.039	0.036	0.038	0.039	0.002	0.006	0.065
cis-1,2-Dichloroethylene	0.036	0.034	0.033	0.031	0.032	0.034	0.033	0.001	0.004	0.044
Chloroform	0.036	0.035	0.034	0.031	0.038	0.032	0.035	0.002	0.007	0.070
1,1,1-Trichloroethane	0.037	0.034	0.035	0.037	0.036	0.036	0.034	0.001	0.004	0.039
Carbon tetrachloride	0.035	0.032	0.029	0.031	0.031	0.032	0.029	0.002	0.006	0.060
1,2-Dichloroethane	0.035	0.034	0.034	0.037	0.038	0.038	0.039	0.002	0.007	0.066
Benzene	0.027	0.027	0.027	0.027	0.028	0.027	0.026	0.000	0.001	0.014
Trichloroethylene	0.029	0.029	0.029	0.028	0.028	0.029	0.029	0.001	0.002	0.017
1,2-Dichloropropane	0.031	0.033	0.032	0.034	0.035	0.032	0.033	0.001	0.004	0.042
Bromodichloromethane	0.073	0.073	0.070	0.075	0.075	0.073	0.075	0.002	0.005	0.053
Toluene	0.023	0.022	0.022	0.023	0.024	0.023	0.022	0.001	0.002	0.021
1,1,2-Trichloroethane	0.034	0.033	0.031	0.034	0.034	0.035	0.033	0.001	0.004	0.036
Tetrachloroethylene	0.027	0.028	0.025	0.028	0.029	0.028	0.029	0.001	0.004	0.038
Dibromochloromethane	0.125	0.119	0.120	0.118	0.121	0.123	0.123	0.003	0.008	0.085
Chlorobenzene	0.034	0.035	0.034	0.034	0.035	0.034	0.034	0.000	0.001	0.013
Ethylbenzene	0.024	0.024	0.024	0.024	0.024	0.024	0.023	0.000	0.001	0.008
m,p-Xylene	0.022	0.023	0.022	0.022	0.022	0.022	0.022	0.000	0.001	0.007
o-Xylene	0.025	0.024	0.024	0.024	0.024	0.025	0.024	0.000	0.001	0.009
Styrene	0.025	0.025	0.026	0.026	0.027	0.026	0.027	0.001	0.003	0.028
Bromoform	0.030	0.031	0.029	0.031	0.030	0.031	0.029	0.001	0.002	0.025
1,4-Dichlorobenzene	0.034	0.032	0.031	0.035	0.032	0.033	0.033	0.001	0.004	0.039
1,2-Dichlorobenzene	0.031	0.032	0.031	0.030	0.030	0.033	0.034	0.001	0.005	0.047
1,2,4-Trichlorobenzene	0.069	0.070	0.066	0.063	0.068	0.069	0.063	0.003	0.009	0.090

Table 6. The results of method detection limit (MDL) and limit of quantification (LOQ) for 28 VOCs.

($\mu g/m^3$)	MDL1	MDL2	MDL3	MDL4	MDL5	MDL6	MDL7	SD	MDL	LOQ
Vinyl chloride	0.049	0.069	0.042	0.044	0.054	0.043	0.034	0.010	0.032	0.318
1,3-Butadiene	0.021	0.032	0.019	0.025	0.027	0.029	0.025	0.005	0.015	0.151
1,1-Dichloroethylene	0.019	0.024	0.013	0.009	0.015	0.009	0.013	0.006	0.018	0.183
Dichloromethane	0.015	0.060	0.043	0.041	0.028	0.008	0.005	0.019	0.061	0.610
MTBE	0.050	0.072	0.050	0.046	0.049	0.054	0.044	0.010	0.030	0.301
trans-1,2-Dichloroethylene	0.037	0.034	0.028	0.027	0.028	0.030	0.030	0.004	0.013	0.126
cis-1,2-Dichloroethylene	0.051	0.053	0.042	0.051	0.045	0.036	0.055	0.006	0.020	0.203
Chloroform	0.045	0.055	0.055	0.048	0.051	0.053	0.054	0.004	0.013	0.129
1,1,1-Trichloroethane	0.053	0.049	0.062	0.048	0.051	0.056	0.044	0.005	0.017	0.168
Carbon tetrachloride	0.043	0.052	0.050	0.043	0.036	0.045	0.040	0.006	0.018	0.185
1,2-Dichloroethane	0.048	0.041	0.051	0.045	0.057	0.050	0.051	0.005	0.017	0.169
Benzene	0.048	0.061	0.057	0.050	0.054	0.052	0.061	0.005	0.015	0.152
Trichloroethylene	0.037	0.035	0.037	0.033	0.031	0.033	0.039	0.002	0.008	0.078
1,2-Dichloropropane	0.045	0.031	0.045	0.043	0.041	0.043	0.043	0.005	0.017	0.169
Bromodichloromethane	0.096	0.102	0.098	0.096	0.102	0.097	0.092	0.003	0.009	0.088
Toluene	0.047	0.052	0.045	0.042	0.040	0.038	0.036	0.005	0.016	0.162
1,1,2-Trichloroethane	0.046	0.058	0.056	0.048	0.047	0.048	0.051	0.005	0.016	0.162
Tetrachloroethylene	0.030	0.030	0.031	0.027	0.031	0.033	0.024	0.002	0.006	0.061
Dibromochloromethane	0.144	0.177	0.155	0.156	0.150	0.155	0.165	0.011	0.036	0.357
Chlorobenzene	0.040	0.043	0.043	0.042	0.041	0.042	0.037	0.001	0.003	0.034
Ethylbenzene	0.027	0.032	0.028	0.031	0.030	0.028	0.031	0.002	0.006	0.065
m,p-Xylene	0.024	0.026	0.024	0.023	0.026	0.027	0.020	0.002	0.005	0.051
o-Xylene	0.030	0.031	0.030	0.028	0.033	0.027	0.028	0.002	0.006	0.061
Styrene	0.015	0.008	0.019	0.011	0.009	0.024	0.010	0.006	0.019	0.192
Bromoform	0.036	0.044	0.039	0.040	0.039	0.036	0.037	0.003	0.009	0.088
1,4-Dichlorobenzene	0.033	0.038	0.035	0.034	0.032	0.032	0.032	0.002	0.008	0.075
1,2-Dichlorobenzene	0.036	0.043	0.035	0.034	0.033	0.033	0.033	0.004	0.012	0.120
1,2,4-Trichlorobenzene	0.064	0.038	0.071	0.070	0.068	0.059	0.067	0.012	0.039	0.391

2.4 Calculation of VOC concentration

As a result of analysis of VOC using GC/MS, the amount of each compound (m) can be confirm. Thus, the convert from amount to concentration considering the sampling rate is required. Therefore, average concentrations (C) is calculated following the equation, which is provided by the manufacturer (RADIELLO®, 2015).

$$C\ (\mu g/m^3) = \frac{m\ (\mu g)}{Q_k\ (mL/min) \times t\ (min)} \times 10^6$$

where m is the mass of analytic adsorbed on the cartridges (μg), t is the sampling periods (min), and Q_k, which is different according to each compound due to mass, volatility, retention time in the air, and so on, is the sampling rate during sampling periods. Actually, the sampling rates at a normal condition (298k) were given by manufacturer (Table 7). In detail, this condition has humidity in the range of 15-90% and wind speed between 0.1-10 m/s. The sampling rate, applied to conditions during sampling periods, can be calculated by the following equation.

$$Q_k = Q_{298} \left(\frac{K}{298}\right)^{1.5} \times 10^6$$

where Q_{298} is the sampling rate at normal condition (298K). K is the absolute temperature during sampling periods. In this study, the sampling rate, applied to conditions during sampling periods, is calculated using these parameters (Q_{298} and absolute temperature during sampling periods).

In addition, although sampling rate of some VOCs is provided by manufacturer, it can be possible that there is no sampling rate for other VOCs. Therefore, the manufacturer also provided another equation for some VOCs.

$$Q_k = D \times \left[\frac{2\pi h}{\ln(\frac{r_d}{r_a})}\right]$$

where D is a diffusion coefficient of each compound (cm^2/min), h is height of the white diffusive body (mm), r_d is radius of the white diffusive body (mm), and r_a is radius of the adsorbing cartridge (mm). Actually, sampling rate of several target compounds (1,1,2-Trichloroethane, 1,1-Dichloroethylene, 1,2,4-Trichlorobenzene, 1,2-Dichlorobenzene, 1,3-Butadiene, Bromodichloromethane, Bromoform, cis-1,2-Dichloroethylene, Dibromochloromethane, trans-1,2-Dichloroethylene, and Vinyl chloride) was calculated in this study.

Table 7. Sampling rates (Q_{298}) of VOCs provided by the manufacture (RADIELLO®, 2015).

	Sampling rate ($mL \cdot min^{-1}$)	**Linearity range ($\mu g \cdot m^{-3} \cdot min$)**	**Uncertainty at 2σ%**
acetone	77	$10{,}000\text{-}600 \cdot 10^6$	7.0
acetonitrile	73	$10{,}000\text{-}6 \cdot 10^6$	8.2
acrylonitrile	75	$1{,}000\text{-}50 \cdot 10^6$	2.2
benzyl alcohol	37	$1{,}000\text{-}800 \cdot 10^6$	6.5
amyl acetate	52	$1{,}000\text{-}800 \cdot 10^6$	3.4
benzene	80	$500\text{-}500 \cdot 10^6$	1.8
bromochloromethane	70	$50{,}000\text{-}1{,}000 \cdot 10^6$	1.4
butanol	74	$1{,}000\text{-}500 \cdot 10^6$	5.0
sec-butanol	64	$1{,}000\text{-}300 \cdot 10^6$	5.2
tert-butanol	62	$1{,}000\text{-}300 \cdot 10^6$	5.5
butyl acetate	60	$1{,}000\text{-}1{,}000 \cdot 10^6$	3.0
2-butoxyethanol	56	$1{,}000\text{-}100 \cdot 10^6$	5.7
2-butoxyethyl acetate	41	$1{,}000\text{-}100 \cdot 10^6$	5.5
carbon tetrachloride	67	$100{,}000\text{-}60 \cdot 10^6$	9.0
cyclohexane	54	$500\text{-}500 \cdot 10^6$	4.5
cyclohexanone	68	$5{,}000\text{-}120 \cdot 10^6$	4.2
cyclohexanol	54	$5{,}000\text{-}120 \cdot 10^6$	4.5
chlorobenzene	68	$1{,}000\text{-}1{,}000 \cdot 10^6$	3.6
chloroform	75	$100{,}000\text{-}60 \cdot 10^6$	9.7
n-decane	43	$500\text{-}1{,}000 \cdot 10^6$	1.1
diaceton alcohol	43	$500\text{-}1{,}000 \cdot 10^6$	4.5
1,4-dichlorobenzene	51	$1{,}000\text{-}1{,}000 \cdot 10^6$	7.7
1,2-dichloroethane	77	$1{,}000\text{-}500 \cdot 10^6$	8.2
1,2-dichloropropane	66	$500\text{-}250 \cdot 10^6$	4.5
dichloromethane	90	$500\text{-}60 \cdot 10^6$	8.7
N,N-dimetylformamide	82	$1{,}000\text{-}200 \cdot 10^6$	14.5
1,4-dioxane	68	$1{,}000\text{-}600 \cdot 10^6$	5.5
n-dodecane	8	$1{,}000\text{-}1{,}000 \cdot 10^6$	4.7
n-heptane	58	$5{,}000\text{-}1{,}500 \cdot 10^6$	3.0
n-hexane	66	$1{,}000\text{-}1{,}000 \cdot 10^6$	2.5
1-hexanol	52	$5{,}000\text{-}120 \cdot 10^6$	5.5
ethanol	102	$10{,}000\text{-}500 \cdot 10^6$	7.5
diethyl ether	78	$5{,}000\text{-}500 \cdot 10^6$	12.0
ethyl acetate	78	$1{,}000\text{-}1{,}000 \cdot 10^6$	1.5
ethylbenzene	68	$1{,}000\text{-}1{,}000 \cdot 10^6$	2.4
2-ethyl-1-hexanol	43	$5{,}000\text{-}500 \cdot 10^6$	10.1
2-ethoxyethanol	55	$500\text{-}50 \cdot 10^6$	6.7
2-ethoxyethyl acetate	54	$10{,}000\text{-}100 \cdot 10^6$	2.5
ethyl-tert-butyl ether (ETBE)	61	$500\text{-}200 \cdot 10^6$	3.0
isobutanol	77	$1{,}000\text{-}300 \cdot 10^6$	2.5
isobutyl acetate	63	$1{,}000\text{-}1{,}000 \cdot 10^6$	5.2
isooctane	55	$500\text{-}1{,}000 \cdot 10^6$	3.2
isopropanol	52	$10{,}000\text{-}400 \cdot 10^6$	12.0
isopropyl acetate	66	$1{,}000\text{-}1{,}000 \cdot 10^6$	9.9
isopropylbenzene	58	$1{,}000\text{-}1{,}000 \cdot 10^6$	2.7
limonene	43	$1{,}000\text{-}1{,}000 \cdot 10^6$	10.0
methanol	125	$10{,}000\text{-}250 \cdot 10^6$	9.2

methyl acetate	80	1,000-1,000·10^6	12.0
methyl-ter-butyl ether (MTBE)	65	500-200·10^6	2.5
methylcyclohexane	66	1,000-1,000·10^6	6.5
methylcyclopentane	70	1,000-1,000·10^6	2.5
methylethylketone	79	1,000-500·10^6	1.6
methylisobutylketone	67	1,000-250·10^6	8.7
methyl metacrylate	68	1,000-500·10^6	2.5
2-methylpentane	70	1,000-1,000·10^6	2.5
3-methylpentane	70	1,000-1,000·10^6	2.5
2-methoxyethanol	35	5,000-100·10^6	11.0
2-methoxyethyl acetate	56	2,000-100·10^6	3.0
1-methoxy-2-propanol	55	1,000-350·10^6	6.0
1-methoxy-2-propyl acetate	60	2,000-350·10^6	6.2
naphtalene	25	1,000-1,000·10^6	7.0
n-nonane	48	1,000-1,000·10^6	5.4
n-octane	53	500-1,000·10^6	3.2
pentane	74	1,000-1,000·10^6	1.9
α-pinene propyl	53	1,000-1,000·10^6	7.0
acetate	65	500-1,000·10^6	7.5
propylbenzene	57	1,000-1,000·10^6	2.9
styrene	61	1,000-500·10^6	3.0
tetrachloroethylene	59	10,000-500·10^6	2.5
tetrahydrofuran	74	2,000-250·10^6	11.0
toluene	74	500-1,000·10^6	1.5
1,1,1-trichloroethane	62	5,000-1,000·10^6	5.5
trichloroethylene	69	5,000-1,000·10^6	2.4
1,2,4-trimethylbenzene	50	500-1,000·10^6	6.6
n-undecane	24	1,000-1,000·10^6	10.0
m-xylene	70	500-1,000·10^6	2.5
o-xylene	65	500-1,000·10^6	2.5
p-xylene	70	500-1,000·10^6	2.5

2.5 Identification of VOC sources

As mentioned previously, large amounts of volatile organic compounds can be emitted from petrochemical, automobile, non-ferrous, shipbuilding industrial complexes due to paints, solvent usages, and vehicle exhausts. Although these kinds of industrial complexes are well known as the main sources of VOCs, almost people do not know which facility accounts for the most emission amount of VOCs exactly. Because of these reasons, identification of VOC sources is required in Ulsan.

In previous studies, many kinds of tools were used for source identification of VOCs such as diagnostic ratios (Toluene/Benzene: T/B and m,p-Xylene/Ethylbenzene: X/E), principle component analysis (PCA) and correlation analysis. Generally, two diagnostic ratios (T/B and X/E) were used to get preliminary information on their sources. T/B ratio provides information on source origin from traffic or non-traffic (Kerchich and Kerbachi, 2012, Sahu and Saxena, 2015). Benzene is a well-known maker of vehicle exhaust (Shi et al., 2015) and toluene which is mainly emitted from evaporation of solvents like paints (Zalel and Yuval, 2008). As an another ratio, X/E indicates aging of VOCs in the atmosphere, because the atmospheric lifetime of benzene and toluene are 12.5 and 2.0 days which mean being stable, and ethylbenzene and xylene are 8 and 3 h (Liu et al., 2008). In addition to this, BTEX ratios such as B/T, B/E, B/X, T/E, T/X, and E/X were also used for source identification (Ho et al., 2004, Lau and Chan, 2003).

Typically, principle component analysis was used to simplify the number of effect factors by extracting target compounds, meteorological data, or criteria air pollutants, and results of the PCA can show that emissions of vehicles, industrial complexes, or gas stations might be influenced in the particular study area (An et al., 2014a, Hsieh et al., 2006, Liu et al., 2008, Ohura et al., 2006). In this study, correlation analysis by SPSS was performed to determine the relationship of each pollutant with parameter related to possible sources (Jaars et al., 2014, Parra et al., 2006), however, most of previous studies focused on only BTEX or a little more compounds (Chan et al., 2002, Ho et al., 2004, Lee et al., 2002b, Tiwari et al., 2010). There are two methods of correlation analysis like Pearson and Spearman correlation analysis. These kinds of analysis can be divided according to distribution of parameters such as measured values, meteorological data, criteria air pollutants or any others. In this study, both methods were applied in order to check of correlation of each parameter and the relationship can be related to the emission sources.

2.6 Risk assessment of VOCs

Volatile organic compounds as well as other organic compounds may generate a variety adverse effects on human health such as diseases, formation of tumors, reproductive defects, or death (An et al., 2014b). If concentration of one target compound is high but toxicity is very low, it is expected that there is no risk of this compound. People can be easily exposed to volatile organic compounds, which has a higher volatility than other pollutants via inhalation, therefore, risk assessment of VOCs should be conducted, especially, in industrial city like Ulsan.

Generally, risk assessment consists of 4 steps including hazard identification, dose-response assessment, exposure assessment, and risk characterization suggested by EPA (Figure 14).

The hazard identification is the process of determining whether or not target compounds can cause adverse health effects. As mentioned previously, several institutes have classified pollutants into a groups (carcinogenic or non-carcinogenic) which can be indicators for chemical toxicity on human health. For example, in case of BTEX, only benzene is classified as carcinogenic compound. Dose-response assessment is used to support the dose-response relationship over the range of observed doses through available data or experiments. The exposure assessment is calculated to measure or estimate the frequency, magnitude, and duration of substances exposure to human in environment. This process takes into account for the exposure pathway and route, which are typically described as intake or uptake. Finally, the risk characterization is the process of decision whether or not risk, calculated by some equations, has potential of adverse effects on human health. According to the following equation, LADD is calculated.

$$\text{LADD} = \frac{\text{C} \times \text{IR} \times \text{ED} \times \text{EF} \times \text{ET}}{\text{BW} \times \text{AT} \times 24}$$

where LADD is the lifetime average daily dose (mg/kg/day), C is the concentration of pollutant ($\mu g/m^3$), IR is inhalation rate (m^3/day), ED is exposure duration (year), EF is exposure frequency (event/year), ET is exposure time (hr/event), BW is body weight (kg), and AT is average time (day). Through this equation, LADD can be calculated by using measured data. Then, in case of carcinogenic compounds, actual risk can be expected by the above mentioned equation. Also, the inhalation slope factor (SF), used for calculation of risk, is provided by US EPA.

US EPA evaluated that cancer risk estimates are acceptable under the range of 1×10^{-6} to 1×10^{-4} whereas the world Health organization (WHO) recommended acceptable risk under the range between 1×10^{-5} and 1×10^{-6} (Bunch et al., 2014, Colman Lerner et al., 2012).

$$\text{Risk} = \text{LADD} \times \text{inhalation Slope Factor (SF)}$$

On the other hand, non-carcinogenic compounds are assessed by hazard quotient (HQ) whether it can give harmful effects to a human. The Reference dose (Rfd), used for calculation of risk, is also given by US EPA. The standard acceptable HQ means that levels being above 1.0 are a potential for health concern, otherwise, those being below 1.0 have no harmful for human (Bunch et al., 2014).

$$\text{HQ} = \frac{\text{LADD}}{\text{Rfd}}$$

In this study, Monte Carlo simulation were used to reduce the uncertainty of risk assessment (Bunch et al., 2014, Civan et al., 2015). It is possible to approach as a probability. Generally, risk assessment was conducted using single value in previous studies (Dumanoglu et al., 2014, Durmusoglu et al., 2010, Okada et al., 2012). Many errors were generated from each parameter to results. On the other hand, a fitted distribution (normal, lognormal, and triangular distributions) is used by the Monte Carlo simulation in this study (Oracle, 2015). Then, results can be calculated as distribution data (Figure 15). The input data can be actually changed according to characteristics of data. Therefore, results of risk assessment need to be evaluated using this simulation (at the worst or safety case).

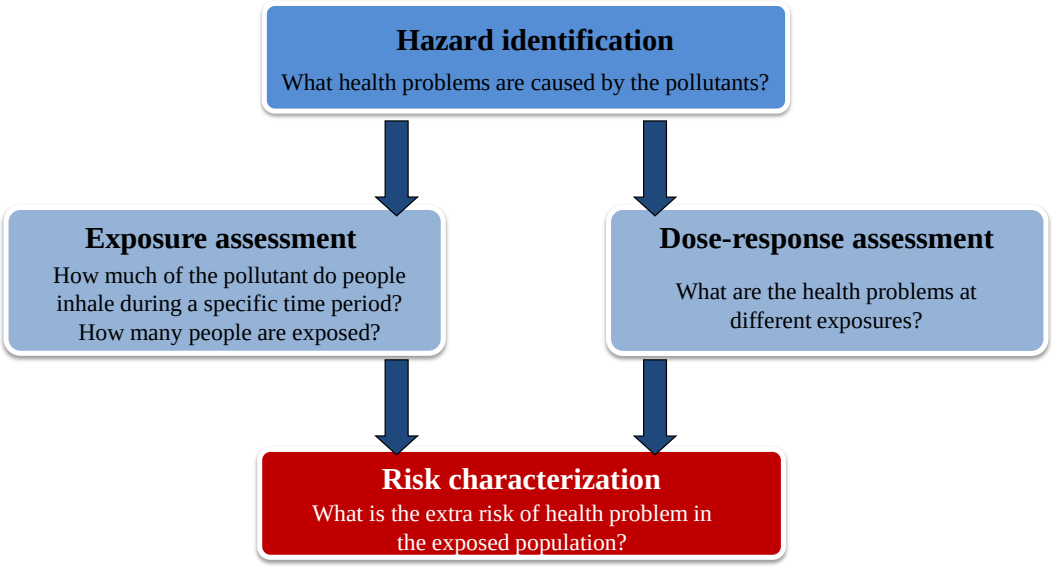

Figure 14. Four steps of risk assessment represented by US EPA.

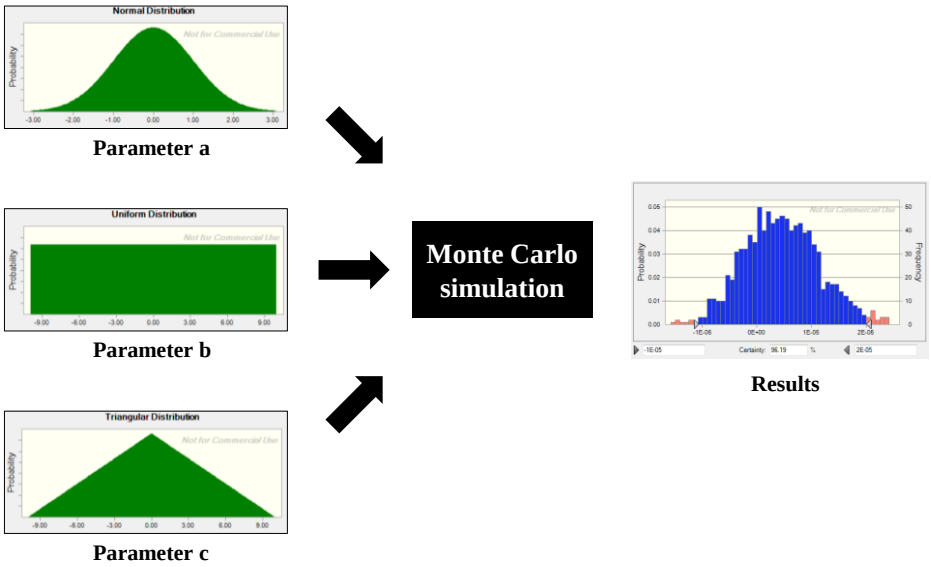

Figure 15. Concept of the Monte Carlo simulation.

Ⅲ. RESULTS AND DISCUSSION

3.1 Meteorological conditions and criteria air pollutants

3.1.1 Meteorological data

Meteorological conditions including wind speed, precipitation, temperature, and humidity are important in the atmospheric environment. Air pollutants are emitted from stacks and then they can, be influenced to other place via wind speed and direction. Precipitation also plays an important role in removing particle matter. Gas phases are easily affected by temperature, volatile organic compounds will volatilize more than other compounds in high temperature season. Therefore, four kinds of meteorological conditions were collected by the Korea Meteorological Administration (KMA, 2015).

Seasonal meteorological conditions were represented in Figure 16 and Table 8. Wind speed ranged between 0.8-5.6 m/s (mean: 2.2 m/s, median: 1.9 m/s) in summer, 0.9-5.5 m/s (mean: 2.0, median: 1.6 m/s) in fall, 0.8-4.5 m/s (mean: 2.3 m/s, median: 2.3 m/s) in winter, 1.0-5.5 m/s (mean: 2.2 m/s, 2.0 m/s) in spring, and 0.8-5.6 m/s (mean: 2.3 m/s, median: 2.1 m/s) during four seasons. Precipitation ranged between 0.2-211.6 mm (mean: 21.1 mm, median: 6.5 mm) in summer, 0.3-49.5 mm (mean: 11.8 mm, 3.8 mm) in fall, 0.1-9.8 mm (mean: 3.5 mm, median: 2.0 mm) in winter, 0.1-33.8 mm (mean: 10.2 mm, median: 6.3 mm) in spring, and 0.1-211.6 mm (mean: 12.3 mm, median: 4.8 mm) during four seasons. Temperature ranged between 20.8-30.3℃ (mean: 25.2℃, median: 25.1℃) in summer, -0.4-19.8℃ (mean: 12.6℃, median: 13.4℃) in fall, -2.4-11.1℃ (mean: 4.2℃, median: 4.1℃) in winter, 10.5-25.5℃ (mean: 18.3℃, median: 18.3℃) in spring, and -3.5-30.3℃ (mean: 14.0℃, median: 14.7℃) during four seasons. Humidity ranged between 57.1-99.8% (mean: 80.4%, median: 80.0%) in summer, 29.0-96.6% (mean: 52.9%, median: 66.6%) in fall, 23.5-88.6% (mean: 52.9%, median: 48.5%) in winter, 28.5-93.5% (mean: 56.8%, median: 54.5%) in spring, and 20.9-99.8% (mean: 62.4%, median: 65.1%) during four seasons.

Wind speed is not a significant difference in all seasons. Precipitation and humidity have a similar pattern, as followed by summer>fall>spring>winter. On the other hand, temperature was the highest in summer, followed by spring, fall, and winter. Consequently, precipitation, temperature, and humidity in summer season were really higher than those of other seasons.

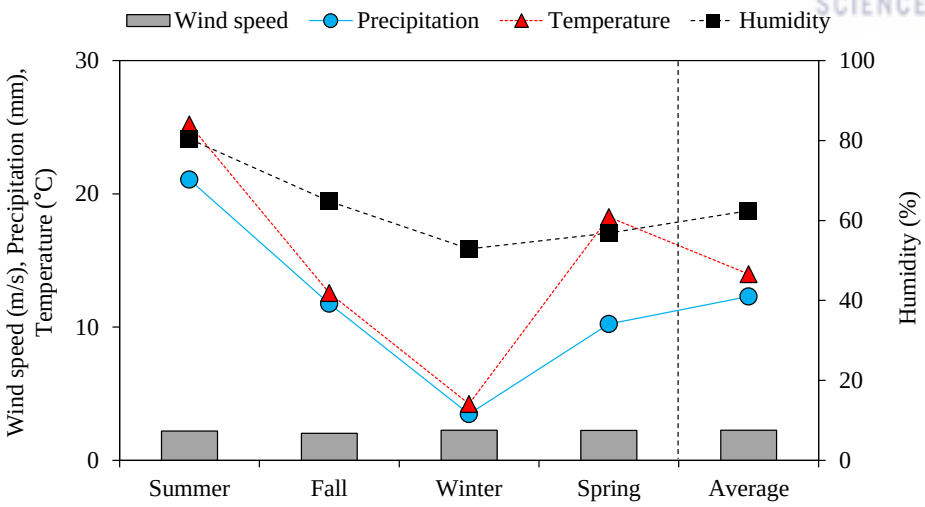

Figure 16. Meteorological conditions including wind speed, precipitation, temperature, and humidity of four seasons in meteorological observatory of Ulsan.

Table 8. Mean and median of meteorological conditions (temperature, precipitation, wind speed, and humidity) during four seasons.

	Summer		**Fall**		**Winter**		**Spring**	
	Mean	**Median**	**Mean**	**Median**	**Mean**	**Median**	**Mean**	**Median**
Temperature (℃)	25.2	25.1	12.6	13.4	4.2	4.1	18.3	18.3
Precipitation (mm)	21.1	6.5	11.8	3.8	3.5	2.0	10.2	6.3
Wind speed (m/s)	2.2	1.9	2.0	1.6	2.3	2.3	2.2	2.0
Humidity (%)	80.4	80.0	64.8	66.6	52.9	48.5	56.8	54.4

Also, the Korea Meteorological Administration provided data of hourly wind speed and directions at eight AWS and one MO. Because sampling sites in this study were related to only three AWS and one MO, the wind data in certain stations were used to understand dispersion of air pollutants and to identify effect of main VOC sources during sampling periods. Especially, passive air samplers were generally deployed during long terms. Therefore, it can be easily effected from wind speed and direction unlike active air sampler.

Figure 17 shows wind roses of four seasons in MO which is representative weather station in Ulsan. The wind roses were drew using wind rose plot (WRPLOT) developed by the lakes environmental

software in Canada (WRPLOT, 2015). Wind directions in summer and spring seasons were dominant with western (W) and eastern (E) winds. Especially, E wind will be largely effected to urban area because most of industrial complexes in Ulsan are located in the east of urban area and along the east coast. Therefore, air pollutants, emitted from most industrial facilities, will move to urban, residential, and rural areas in summer and spring seasons. On the other hand, wind directions in fall and winter seasons were mainly northwestern (NW) wind, therefore, air pollutants in fall and winter seasons will directly move to the east sea.

However, Figure 17 shows only wind direction of MO in Ulsan, and it cannot be applied to all of the sampling sites in this study. Therefore, to exactly interpret, wind roses of four AWS and average are represented in Figure S1.

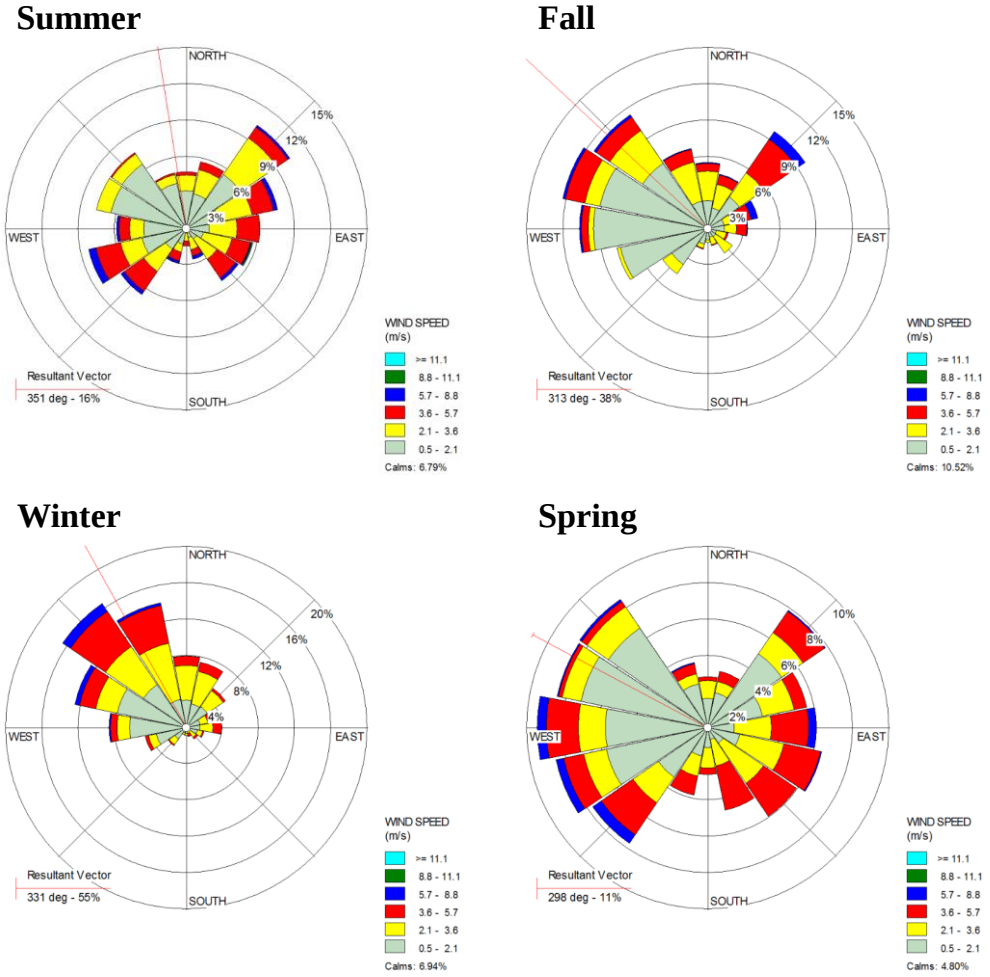

Figure 17. Wind rose of four seasons in meteorological observatory of Ulsan.

3.1.2 CAPs data

CAPs are also one of the important factors to understand atmospheric environment in the study area. As mentioned previously, five kinds of CAPs including PM_{10}, SO_2, O_3, NO_2, and CO were observed by the UIHE (UIHE, 2015). There are 14 sampling sites which are divided into urban, residential, commercial, and industrial areas (Figure 18). US EPA established National Ambient Air Quality Standards (NAAQS) for five pollutants which were regarded as harmful to human health and the atmospheric environment. The Clean air Act also requires US EPA to periodically update the standards of CAPs to make sure that they supply acceptable human health (Buckley and Farraj, 2015).

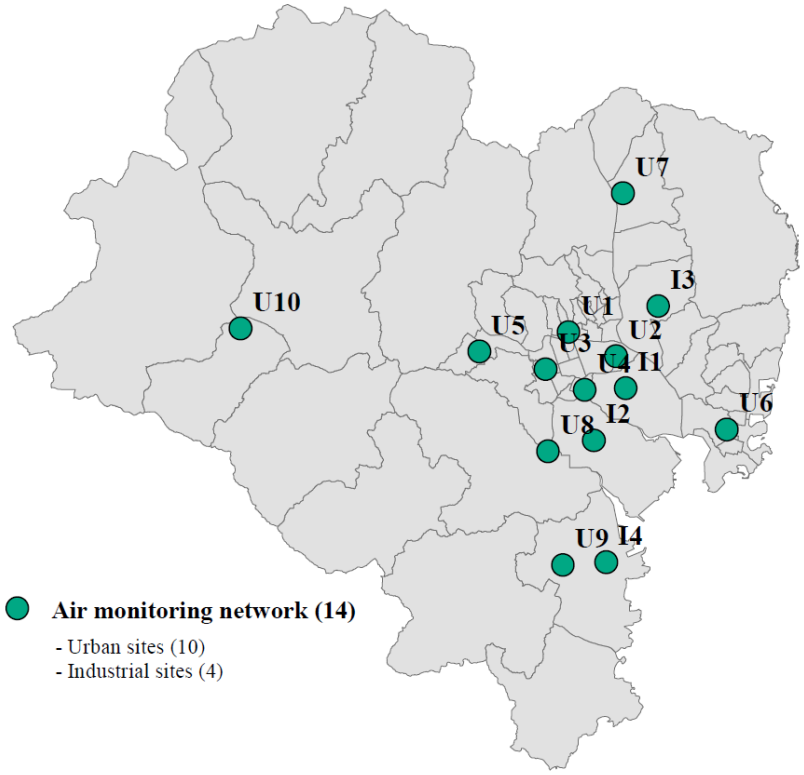

Figure 18. The monitoring sites for air, heavy metal, and acid rain monitoring operated by Ulsan Institute of Health and Environment (UIHE).

O_3, as a secondary pollutant, is mostly produced by photochemical reactions of NO_X and VOCs in the atmosphere. SO_2 is mainly emitted from local industries used by heavy oil and coal in developed countries (Clarke et al., 2014). Lager amount vehicles, power plants, and biomass burning based on combustion sources may be a major emission source of NO_2 and CO (Buckley and Farraj, 2015). Particulate matter (PM) is a multiple mixture of very small particles, and they consist of inorganic

(ammonium, sulphates, and nitrates) and organic (calcium, chloride, and sodium), as well as elemental carbon and metals (copper, zinc, and cadmium) (Sanchez-Soberon et al., 2015). Also, PM can be emitted from both natural and anthropogenic sources, for instance coal combustion, residential heating, and sand storm, which are well known as the main source of PM (Sanchez-Soberon et al., 2015).

To investigate pollution levels of CAPs, supplied by the UIHE, sampling sites of the UIHE and this study were matched (Figure 19). Concentration of CO was especially the highest at I2 (Yeocheon) site in four seasons (summer: 0.6 ppm, fall: 0.9 ppm, winter: 1.1 ppm, spring: 0.7 ppm, and annual average: 0.8 ppm). Many kinds of combustion sources may probably be located in I2 site. Levels of SO_2 at industrial areas (I1-I6) were much higher than those of urban areas in summer and spring seasons. Large amount of pollutants would be emitted from all of the industrial complexes in summer and spring seasons, it could be effected to urban areas. Levels of O_3 in spring were much higher than those of other seasons, and also, concentrations of NO_2 in this season have a significant difference with those of O_3 unlike other seasons. It is possible to expect that concentrations of VOCs would be shown in spring season rather than those of other seasons. Levels of PM in winter and spring showed a higher trend than those of summer and fall. Emission amount of PM in winter account mainly for domestic house heating due to cold weather (Wang et al., 2014), and yellow dust in case of South Korea would be mainly generated in spring season.

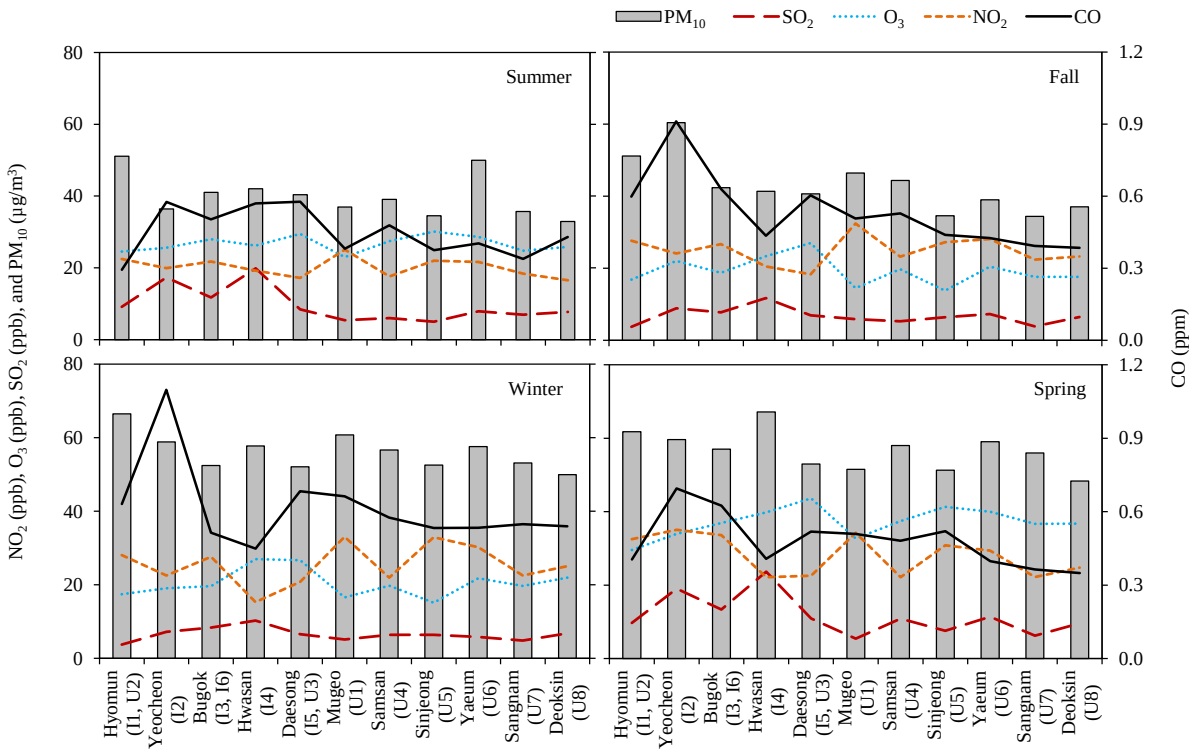

Figure 19. Five CAPs data (PM_{10}, SO_2, O_3, NO_2, and CO) at 11 sites measured by UIHE during four seasons in Ulsan.

In addition, the Korea Ministry of Environment have been investigating periodically VOCs at two sites (urban: Sinjeong, industrial: Yeocheon). The target compounds are 13 VOCs including benzene, carbon tetrachloride, chloroform, ethylbenzene, m,p-xylene, o-xylene, styrene, tetrachloroethylene, toluene, trichloroethylene, 1,1,1-trichloroethane, 1.1-dichloroethane, and 1,3-butadiene. Therefore, concentration of VOCs, which are selected based on 13 VOCs, in this study were compared with those of the KME at same sampling sites during four seasons (Figure 20).

In this study, concentrations of VOCs at urban site were quite higher than those at UIHE. Especially, ethylbenzene, m,p-xylene, o-xylene, and toluene were much higher in summer, winter, and spring. In case of 1,3-butadiene, the concentration in this study was not detected in all of the seasons, on the contrary, those of the UIHE were pretty detected in all of the seasons. In comparison with industrial site, concentration of toluene in this study was much higher than those of the UIHE in all of the seasons, and concentration of m,p-xylene in the UIHE was highest over four seasons and sites. Overall, concentration of individual VOCs during fall represented higher value than other seasons in the UIHE, however, the representation time of this study was spring.

In conclusion, most of patterns for VOC concentrations at urban and industrial sites were pretty similar with each other. However, there were quite different concentration of individual concentration between the UIHE and this study. Because VOC monitoring in the UIHE was conducted using active air sampler during 24 hour, on the contrary, passive air sampler was used in this study during approximately a month.

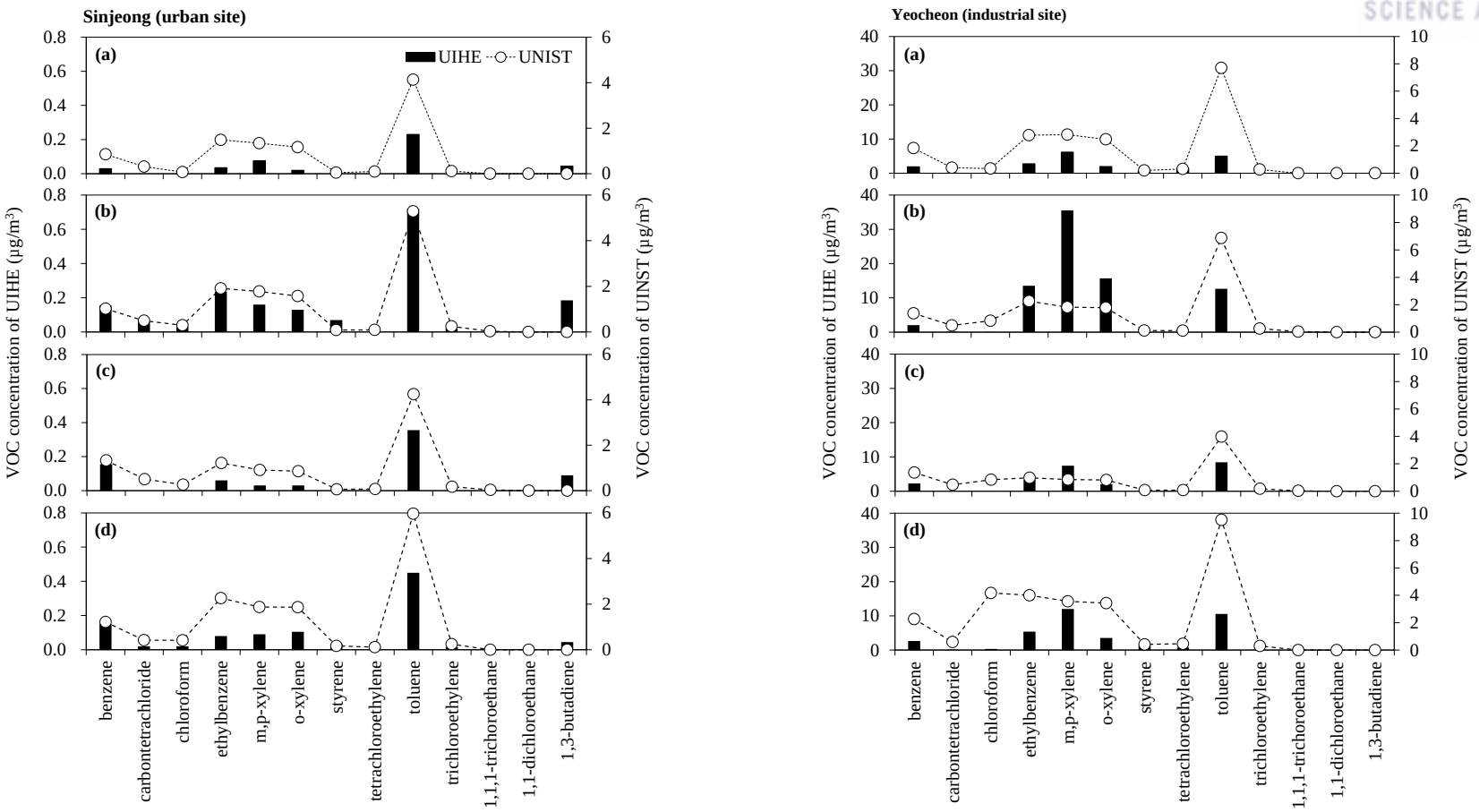

Figure 20. Comparison between UIHE and UNIST for concentration of 13 VOCs during four seasons. (a) Summer, (b) fall, (c) winter, and (d) spring at urban and industrial sites.

3.2 Levels and patterns of VOCs

3.2.1 Seasonal variations of VOC concentration

In this study, VOC monitoring was conducted during four seasons. The concentration of total VOCs ranged from 0.0-9.4 μg/m^3 (mean: 1.1 μg/m^3, median: 0.28 μg/m^3) in summer, 0.0-11.0 μg/m^3 (mean: 1.3 μg/m^3, median: 0.54 μg/m^3) in fall, 0.0-6.3 μg/m^3 (mean: 0.9 μg/m^3, median: 0.51 μg/m^3) in winter, and 0.0-11.8 μg/m^3 (mean: 1.6 μg/m^3, median: 0.77 μg/m^3) in spring (Figure 21). Average concentration of total VOCs was highest in spring, followed by fall, summer, and winter. Actually, wind direction of Ulsan in winter was dominant with northwestern wind, thus, VOCs emitted from industrial complexes located along the coast, might be not effect to sampling sites.

On the other hand, results of statistical analysis (rank sum test) between spring and summer, fall and winter, and spring and winter showed a statistically significant difference, indicating *p* value were 0.020, 0.002, and 0.001, respectively. Generally, seasonal concentrations of VOCs were highest in summer or spring because VOCs would be volatilized well due to higher temperature during summer than those of other seasons. Also, other studies reported that concentrations of VOCs in winter or fall could show the highest value due to calm conditions and high atmospheric stability, limiting dilution of VOCs (Dumanoglu et al., 2014). According to results of other studies, seasonal concentration of total VOCs represented as follows: spring>summer>winter>autumn at rural areas (Zhang et al., 2014), fall>spring>summer>winter at industrial areas (Dumanoglu et al., 2014), summer>spring>fall>winter at industrial areas (An et al., 2014a), or winter>spring>fall>summer at urban areas (Fanizza et al., 2014). Unlike these literatures, concentration of seasonal VOCs in Ulsan showed that there is no a statistically significant difference. This result indicate that Ulsan show a significant industrial property, continuously emissions of VOCs were from industrial facilities.

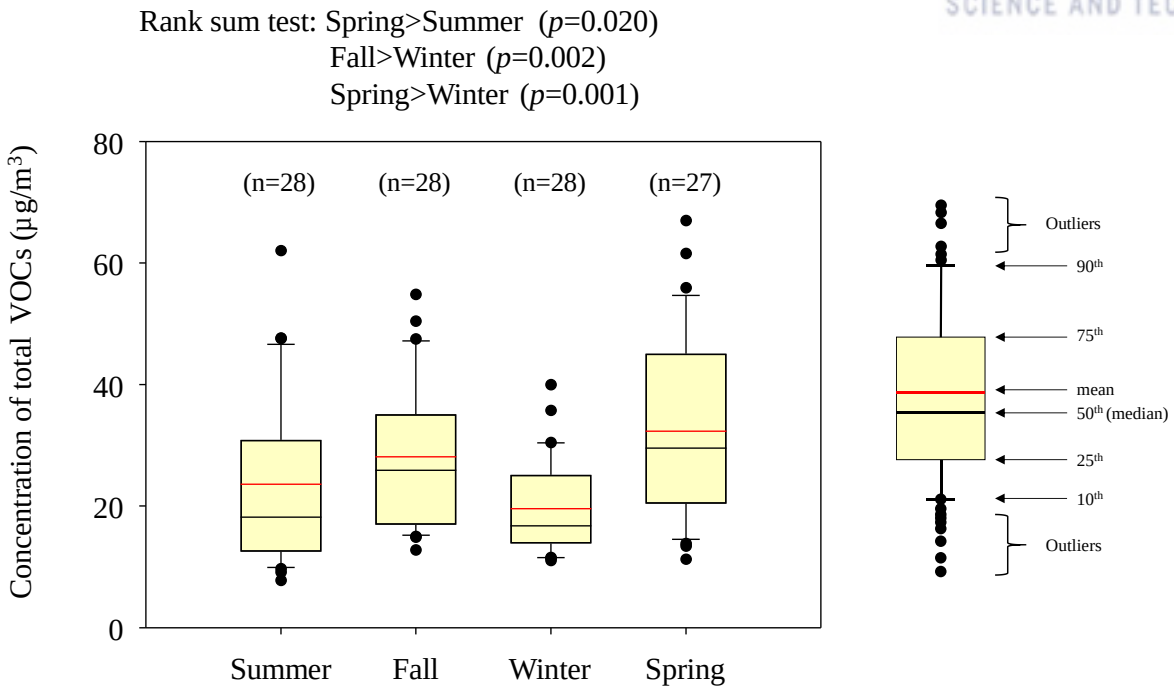

Figure 21. Results of concentrations and rank sum test of total VOCs at 14 sampling sites in Ulsan over four seasons.

3.2.2 Concentration of target compounds

The concentration of five compounds were highest among the target compounds based on mean concentration. As a result of the concentration by four seasons, the highest concentration in summer was toluene, and then followed by m,p-xylene, ethylbenzene, o-xylene, and benzene (8.3 μg/m^3, 3.3 μg/m^3, 3.1 μg/m^3, 2.8 μg/m^3, and 2.7 μg/m^3, respectively) (Figure 22). In case of fall, the highest level was toluene, and followed by ethylbenzene, m,p-xylene, o-xylene, and benzene (9.6 μg/m^3, 3.3 μg/m^3, 3.0 μg/m^3, 2.8 μg/m^3, and 1.8 μg/m^3, respectively). Results of winter showed that levels of toluene, vinyl chloride, benzene, ethylbnezne, and m,p-xylene were 5.9 μg/m^3, 2.1 μg/m^3, 1.8 μg/m^3, 1.8 μg/m^3, and 1.7 μg/m^3, respectively. Also, concentration of toluene, ethylbenzene, m,p-xylene, o-xylene, and benzene in spring were 9.8 μg/m^3, 4.6 μg/m^3, 4.0 μg/m^3, 3.8 μg/m^3, and 2.6 μg/m^3, respectively.

Consequently, among these compounds, mean concentration of toluene was the highest in all of the seasons, and then followed by benzene, ethylbenzene, m,p-xylene, o-xylene except for vinyl chloride in winter. Actually, high concentration of vinyl chloride were detected in previous study which is studied in Ulsan (Na et al., 1998), and this chemicals are usually used to produce the polyvinyl chloride (PVC) in petrochemical facilities or landfills (Jeon et al., 2003), and 1,1-dichloroethylene, bromodichloromethane, and chlorobenzene were not detected in all of the seasons. In addition,

dibromochloromethane in fall, winter, and spring, 1,4-dichlorobenzene in winter and spring, tran-1,2-dichloroethylene, vinyl chloride, and 1,3-butadiene in summer, and 1,1,1-trichloroethane, 1,2,4-trichlorobenzene, 1,2-dichlorobenzene in spring were not detected.

1,3-butadiene was detected in fall, winter, and spring at I3 site, and it was detected at I1 in fall. This compound was used as a chemical feedstock in some processes involving petroleum refining, lead smelting, producing rubbers, and wastewater treatment (Carrieri et al., 2014). 1,3-Butadiene also detected at I3 site, which is located in petrochemical industrial complex, and I1 site would be influenced by nearby automobile and waste water treatment complexes. Also, concentrations of styrene and 1,2-dichloropropane at I3 site were much higher than those of other sites in all of the seasons. It is indicated that these two compounds might have similar emission sources, and this result supported that phenomena.

Concentration of annual average for target compounds are shown in Figure 23. Toluene was expectably the highest concentration in annual average (8.4 μg/m^3), followed by ethylbenzene, m,p-xylene, o-xylene, and benzene (3.2 μg/m^3, 3.0 μg/m^3, 2.7 μg/m^3, and 2.2 μg/m^3), respectively. 1,1-Dichloroethylene, bromodichloromethane, and chlorobenzene were not detected during four seasons. In addition, 1,1-dichloroethylene, bromodichloromethane, and chlorobenzene were not detected at all of the sampling sites.

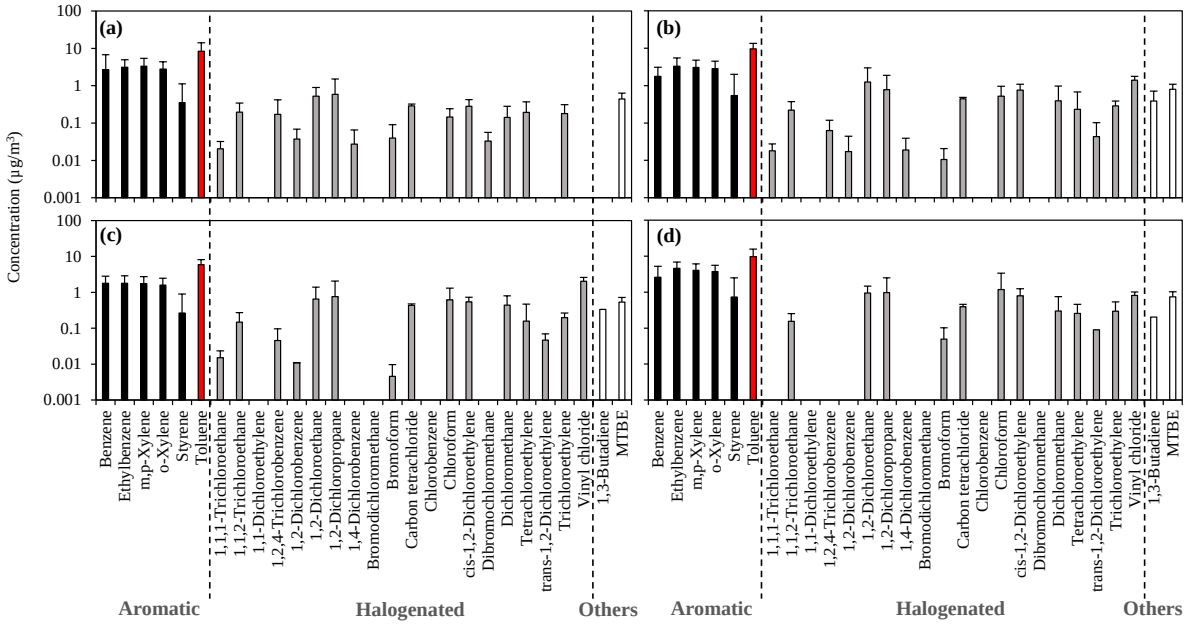

Figure 22. Concentration of individual target compound during four seasons. (a) Summer, (b) fall, (c) winter, and (d) spring.

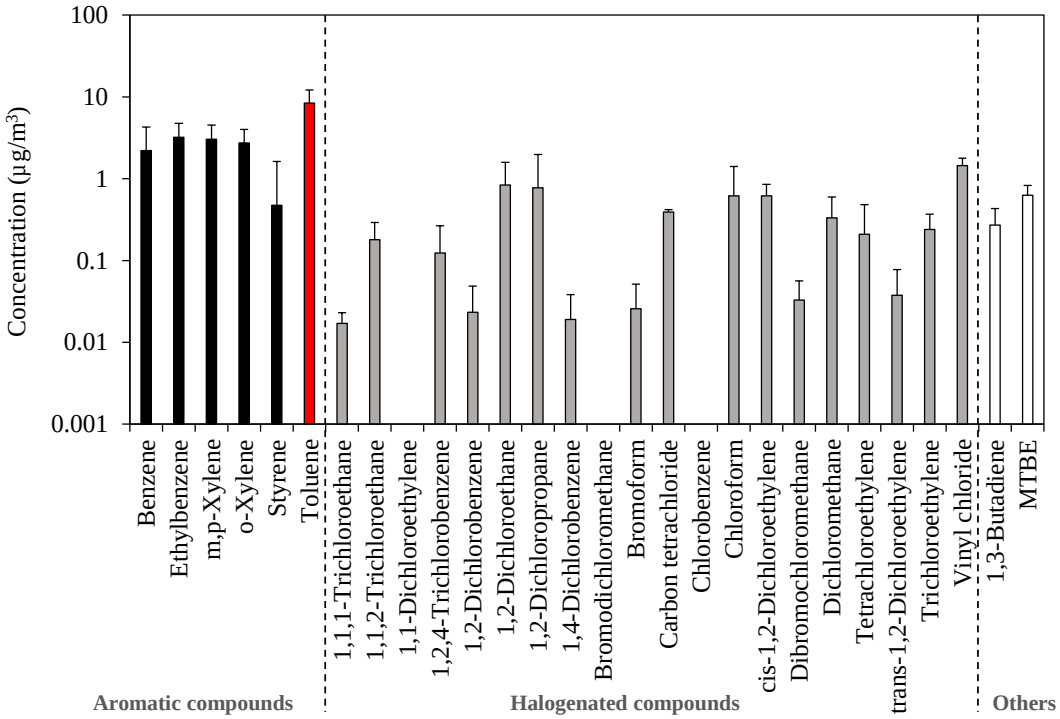

Figure 23. Annual concentration of each target compound collected 14 sites in Ulsan.

3.2.3 Fractions of three groups

The target compounds (28 VOCs) were divided into three groups as aromatic, halogenated, and others groups. The annual concentration and fraction of three groups were depicted Figure 24(a). Among three groups, aromatic group was the highest concentration and had a large fraction as 75%, followed by halogenated groups (22%) and other groups (3%). Each group has a statistically significant difference (p=<0.001) based on the t-test using sigma-plot. The aromatic group including benzene, toluene, ethylbenzene, m,p-xylene, o-xylene, and styrene accounted for 75% of total VOCs based on the annual concentration. In case of fraction for three groups according to the seasons, aromatic group, halogenated group, and other group show as followed: 86%, 12%, and 2% in summer, 74%, 23%, and 3% in fall, 66%, 31%, and 3% in winter, and 79%, 19%, and 2% in spring, respectively. Fraction of aromatic group was highest in summer and lowest in winter. The reasons of high fraction of aromatic group are because of BTEX which were over 80%.

As shown in Figure 24(b), among the 6 VOCs in aromatic group, toluene was the highest fraction, followed by ethylbenzene, m,p-xylene, o-xylene, benzene, and styrene (42%, 16%, 15%, 14%, 11%, and 2%, respectively) in annual average. In addition, seasonal fraction of aromatic group accounted for

40%, 15%, 16%, 14%, 13%, and 2% in summer, 46%, 16%, 14%, 13%, 8%, and 3% in fall, 45%, 14%, 13%, 12%, 14%, and 2% in winter, and 38%, 18%, 16%, 15%, 10%, and 3% in spring (Figrue S2-S5). These results were same with previous studies indicating large fraction of BTEX among atmospheric VOC (Kerchich and Kerbachi, 2012, Miller et al., 2011). Consequently, monitoring and management of BTEX among VOCs are required.

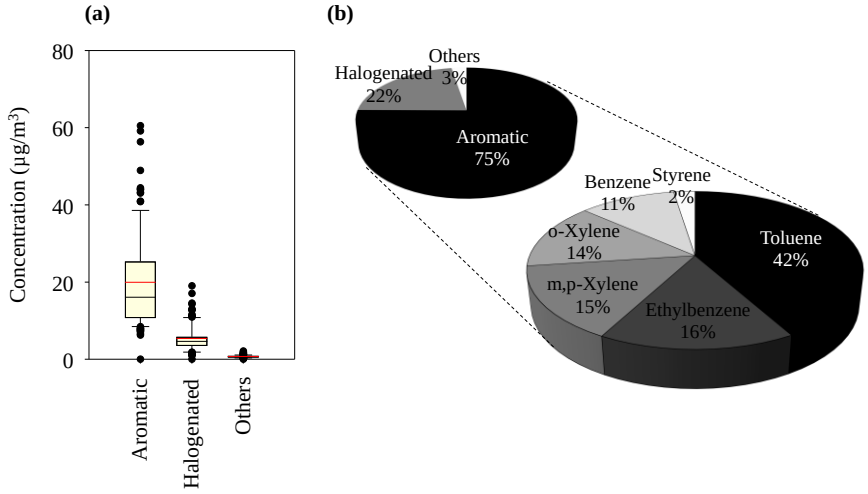

Figure 24. The concentration of three groups (a) and fraction of detailed aromatic group based on the annual average levels (b).

3.2.4 Fractions of BTEX

Figure 25 show fraction of benzene, ethylbenzene, m,p-xylene, o-xylene, and toluene at each sampling site in summer, fall, winter, and spring. The fraction of Toluene represented the largest value among BTEX at all of the sampling sites. Exceptionally, fractions of toluene at I3 in winter, I4 in summer, and I6 sites in summer and spring (29, 30, 27, and 28%) were similar with or lower than that of benzene (24, 29, 36, and 28%). I3 and I6 sites would be influenced by vehicle emissions which will be explained in the next part. In case of I4 site, located in non-ferrous industrial complex, US EPA actually reported that benzene are primarily emitted from production in coke ovens such as non-ferrous metal manufacture, coal, and ore mining (EPA, 1993). The reason of large fraction of benzene might be related to the local property, which is located in non-ferrous industrial complex.

The levels of Ethylbenzene and m,p-xylene at I5 and U3, located nearby shipbuilding and heavy industrial complexes in Ulsan were higher than those of other sampling sites in all of the seasons (summer: 23% and 20%, 25% and 21%, fall: 22% and 17%, 19% and 16%, winter: 21% and 17%, 18% and 16%, and spring: 25% and 19%, 27% and 20%). As mentioned in introduction part, emission

amount of chemicals provided by Korea Ministry of Environment showed that shipbuilding and heavy industrial complexes, nearby two sites (I5 and U3), had the highest emission amounts. On the other hand, o-xylene at each sampling sites was not a significant difference during sampling periods.

Fraction of BTEX, based on the annual average concentration, has similar patterns with those of four seasons as shown previously. Each compound ranged 4-25% (mean: 11%, median: 11%) for benzene, 35-54% (mena:44%, median: 44%) for toluene, 13-23% (mean: 16%, median:16%) for ethylbenzene, 12-19% (mean: 15%, median: 15%) for m,p-xylene, and 10-18% (mean: 14%, median: 14%) for o-xylene in annual average, respectively. The fraction of the Toluene also accounted for the largest value among BTEX, like seasonal results, benzene was a little high at I3, I4, and I6 sites. These results were depicted in Figure 26.

In addition, concentration of BTEX in this study was compared with those in previous studies (Figure 27), and concentrations of individual and total VOCs were represented in Table 9. As expected, the concentration of toluene was highest among BTEX in all of the previous, and these concentrations in Canada (Miller et al., 2012) and USA (Chung et al., 2009) were overall lower than others, and Italia (Roukos et al., 2009), Finland (Helle´n et al., 2002), Algeria (Kerchich and Kerbachi, 2012), and Turkey (Dumanoglu et al., 2014) were similar with each other and this study. Also, there are three studies of BTEX in Korea. Each concentration of BTEX was highest in 1997 followed by 2009 and 2014. It show that concentration of BTEX has a decreasing pattern. These kinds of trends can be possible because they conducted monitoring of VOCs during different periods and using active air samplers.

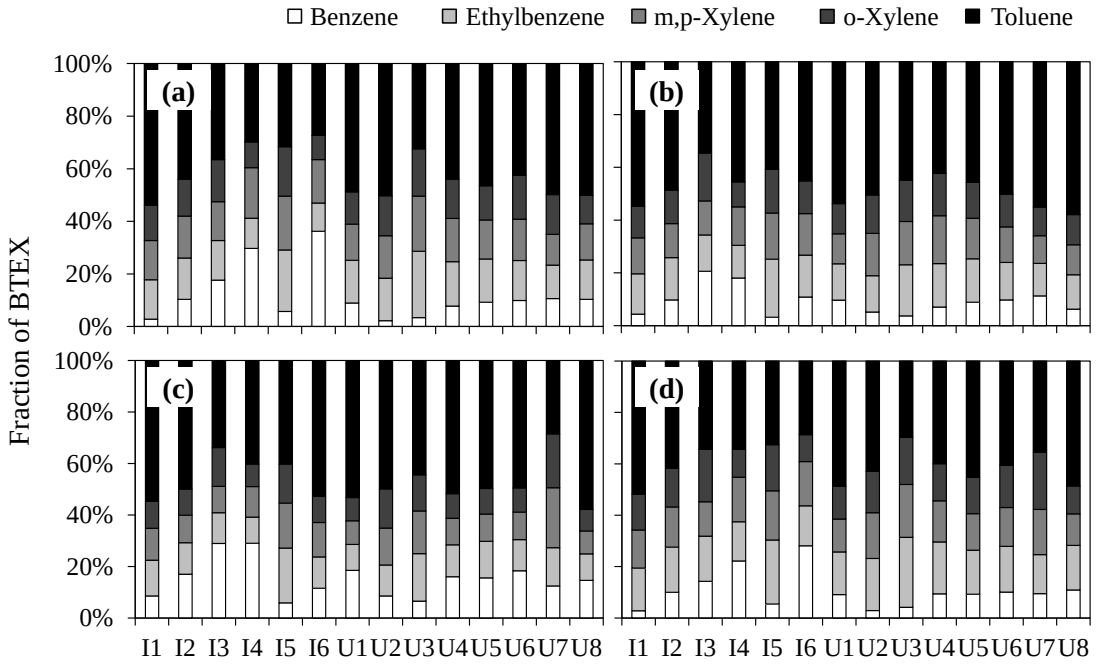

Figure 25. Fraction of BTEX at each sampling site. (a) Summer, (b) fall, (c) winter, and (d) spring.

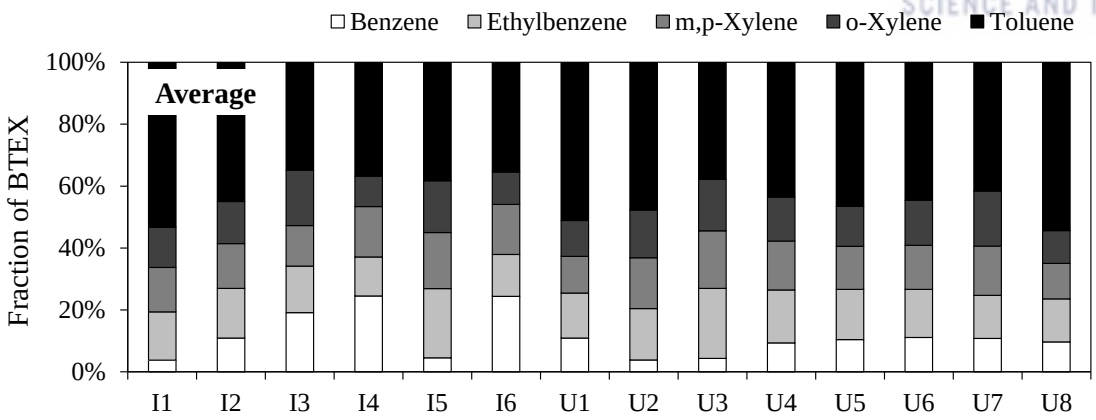

Figure 26. Fraction of BTEX at each sampling site based on the annual average concentration.

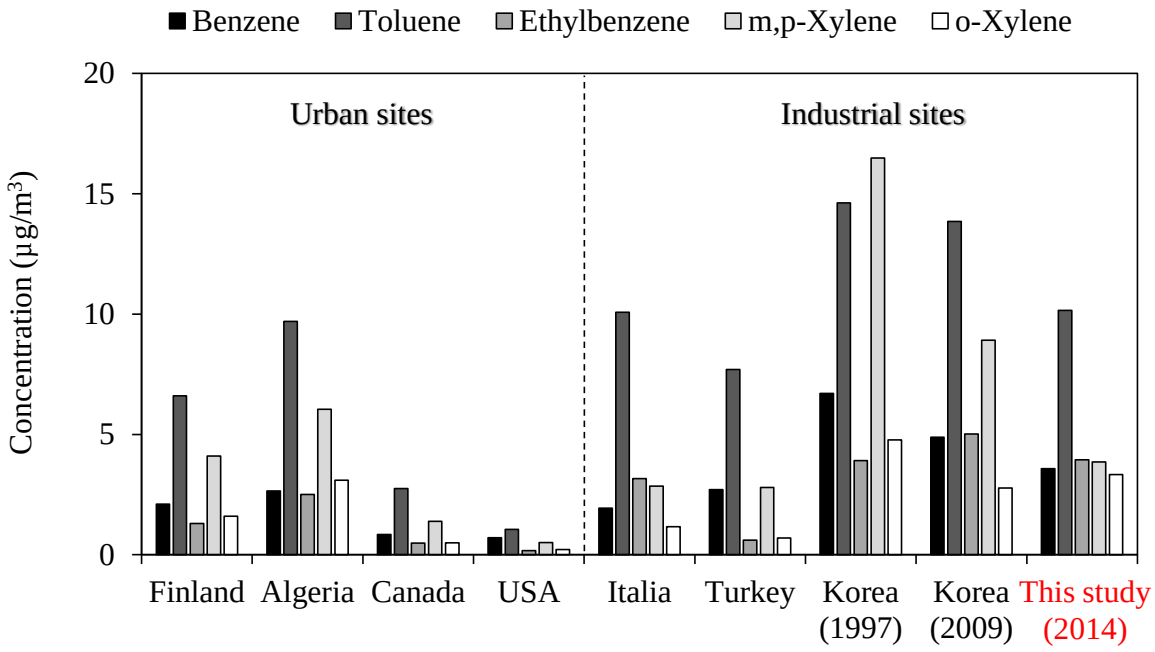

Figure 27. Comparison of concentration of benzene, toluene, ethylbenzene, m,p-xylene, and o-xylene in Italia, Finland, Algeria, Canada, USA, Turkey, Korea, and this study.

Table 9. Mean, median, and standard deviation of concentration for target compounds in four seasons.

Compounds (µg/m^3)	Summer			Fall			Winter			Spring		
	Mean	Median	SD	Mean	Median	SD	Mean	Median	SD	Mean	Median	SD
Benzene	2.68	1.04	4.05	1.77	1.19	1.30	1.79	1.36	1.04	2.59	1.50	2.67
Ethylbenzene	3.14	2.91	1.80	3.30	2.70	2.20	1.78	1.58	1.11	4.58	4.05	2.28
m,p-Xylene	3.33	2.81	2.10	3.03	2.82	1.76	1.74	1.60	1.02	4.03	3.65	2.10
o-Xylene	2.77	2.54	1.62	2.83	2.29	1.67	1.59	1.44	0.90	3.76	3.55	1.86
Styrene	0.35	0.13	0.77	0.54	0.13	1.46	0.27	0.10	0.63	0.73	0.27	1.77
Toluene	8.32	6.77	5.73	9.59	9.19	3.88	5.89	5.16	2.27	9.80	7.31	5.92
1,1,1-Trichloroethane	0.02	0.02	0.01	0.02	0.02	0.01	0.01	0.02	0.01			
1,1,2-Trichloroethane	0.19	0.14	0.15	0.22	0.15	0.15	0.15	0.10	0.12	0.15	0.12	0.10
1,1-Dichloroethylene												
1,2,4-Trichlorobenzene	0.17	0.10	0.25	0.06	0.04	0.06	0.05	0.02	0.05			
1,2-Dichlorobenzene	0.04	0.04	0.03	0.02	0.01	0.03	0.01	0.01				
1,2-Dichloroethane	0.53	0.32	0.37	1.24	0.54	1.74	0.65	0.30	0.74	0.95	0.70	0.52
1,2-Dichloropropane	0.59	0.30	0.92	0.77	0.37	1.10	0.76	0.29	1.31	0.97	0.45	1.53
1,4-Dichlorobenzene	0.03	0.01	0.04	0.02	0.01	0.02						
Bromodichloromethane												
Bromoform	0.04	0.02	0.05	0.01	0.01	0.01	0.00	0.00	0.01	0.05	0.03	0.05
Carbon tetrachloride	0.29	0.29	0.03	0.45	0.46	0.04	0.43	0.44	0.04	0.39	0.39	0.07
Chlorobenzene												
Chloroform	0.15	0.11	0.10	0.52	0.33	0.44	0.62	0.28	0.69	1.18	0.39	2.20
cis-1,2-Dichloroethylene	0.28	0.26	0.14	0.76	0.67	0.33	0.54	0.49	0.19	0.79	0.64	0.45
Dibromochloromethane	0.03	0.03	0.02									
Dichloromethane	0.14	0.11	0.14	0.39	0.15	0.58	0.44	0.30	0.36	0.30	0.10	0.45
Tetrachloroethylene	0.19	0.14	0.18	0.23	0.10	0.44	0.16	0.07	0.32	0.26	0.17	0.20
trans-1,2-Dichloroethylene				0.04	0.04	0.06	0.05	0.05	0.02	0.09	0.09	
Trichloroethylene	0.18	0.14	0.13	0.29	0.25	0.10	0.20	0.16	0.07	0.29	0.24	0.24
Vinyl chloride				1.39	1.30	0.37	2.03	2.03	0.56	0.81	0.81	0.20
1,3-Butadiene				0.39	0.39	0.33	0.33	0.33		0.20	0.20	
MTBE	0.44	0.39	0.19	0.80	0.82	0.29	0.53	0.53	0.19	0.74	0.72	0.29
$\sum_{28}$VOC	23.91			28.68			20.01			32.68		

3.2.5 Concentration of total VOCs at the sampling sites

Concentration of total VOCs and BTEX in annual average at each sampling site were compared as shown in Figure 28, and those of seasonal data were represented in Figure S6-S9. Average concentration of total VOCs was 34.5 $\mu g/m^3$ at all industrial sites and 20.7 $\mu g/m^3$ at all urban sites, concentration of BTEX was 24.9 $\mu g/m^3$ at all industrial sites and 15.7 $\mu g/m^3$ at urban sites during four seasons. Concentrations of total VOCs were mainly high at industrial sites and low at urban sites during all of sampling periods, except for I2 and U2. The I2 site, which is located in petrochemical industrial complex, and U2 site, which is located nearby automobile industrial complex, had an unexpected result. Thus, these sampling sites might be influenced from industrial facilities.

As an industrial area, the concentration at I2 site showed lower concentration of total VOCs than that of other industrial sites. It might be effected by wind direction, distance from industrial facilities, and so on. The reasons will be explained in a next part. Although U2 site is classified as an urban site, high concentrations of VOCs were frequently represented as much as industrial area due to effect of industrial area. In addition, the concentration at U2 site was relatively high in summer and spring, or low in fall and winter, this patterns was shown at I1 site which is located in automobile industrial complex. Similarly, I5 and U3 sites showed a similar pattern like I1 and U2 because of shipbuilding and heavy industrial complexes. Concentration of total VOCs at U1 site was smallest in all of four seasons, because this site is farthest away from the industrial complexes among sampling sites in Ulsan.

In comparison with concentration of total VOCs and BTEX, slightly different patterns were shown at I3 and I4 sites. It means that there are the effects of other compounds as well as BTEX. As mentioned previously, concentration of styrene, 1,2-dichloroethane, and 1,2-dichloropropane at I3 site were somewhat higher than those of other sites. Unlike I3 site, chloroform and cis-1,2-dichloroethylene were detected at I4 site at a little higher than other sites. It might probably be due to effects of similar emission sources.

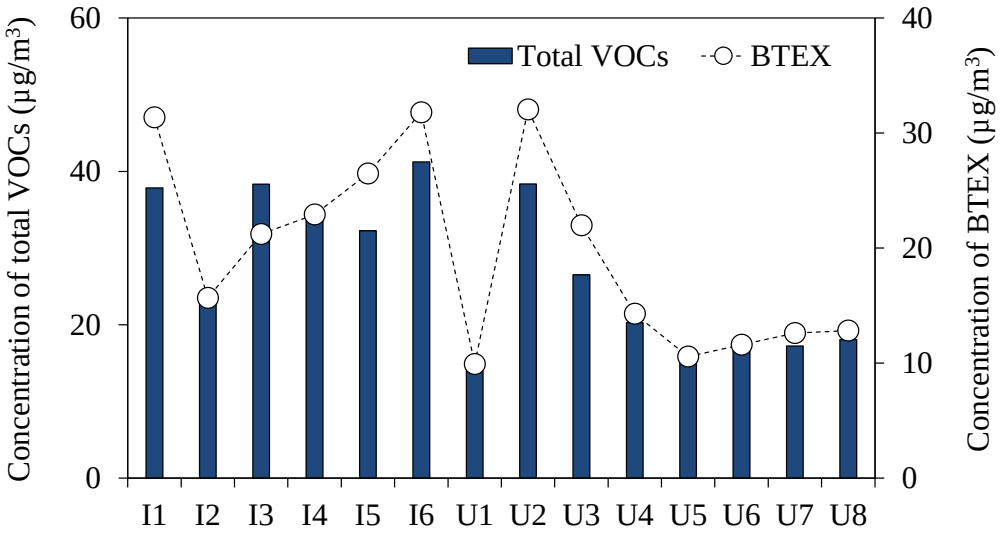

Figure 28. Concentration of total VOCs and BTEX at each sampling site in annual average.

Total 14 sampling sites of Ulsan in this study were divided into 6 industrial (I1-I6) and 8 (U1-U8) urban sites. Seasonal and annual average of VOC concentrations of industrial and urban sites were compared and depicted in Figure 29. Concentration of total VOCs in industrial sites ranged from 15.2-47.9 μg/m^3 (mean: 30.7 μg/m^3, median: 28.9 μg/m^3) in summer, 17.4-55.2 μg/m^3 (mean: 37.7 μg/m^3, median: 35.4 μg/m^3) in fall, 14.1-40.3 μg/m^3 (mean: 24.7 μg/m^3, median: 23.8 μg/m^3) in winter, 22.7-67.3 μg/m^3 (mean: 43.8 μg/m^3, median: 47.0 μg/m^3) in spring, and 14.1-67.3 μg/m^3 (mean: 34.1 μg/m^3, median: 31.4 μg/m^3) in annual average. Extremely high concentration (outlier) was detected at I6 in summer and spring, and the concentration at I5 also shown the highest value in fall and winter.

Concentration of total VOCs in urban sites ranged from 8.0-62.3 μg/m^3 (mean: 18.7 μg/m^3, median: 13.2 μg/m^3) in summer, 13.0-37.0 μg/m^3 (mean: 21.5 μg/m^3, median: 19.8 μg/m^3) in fall, 11.4-36.1 μg/m^3 (mean: 16.3 μg/m^3, median: 14.5 μg/m^3) in winter, 11.5-61.8 μg/m^3 (mean: 24.9 μg/m^3, median: 21.5 μg/m^3) in spring, and 8.0-62.3 μg/m^3 (mean: 20.4 μg/m^3, median: 17.1 μg/m^3) in annual average. The highest concentration (outlier) was detected at U2 in summer, winter, spring, and also U3 site shown the high concentration in fall.

In addition, BTEX concentration of industrial and urban sites is represented in Figure S10 like total VOCs (Figure 29). In comparison with BTEX and total VOCs, a lot of difference was not found by patterns in all of the seasons and annual average. However, as a result of t-test and rank sum test, concentrations at industrial sites were higher than those at urban sites in both BTEX and total VOCs.

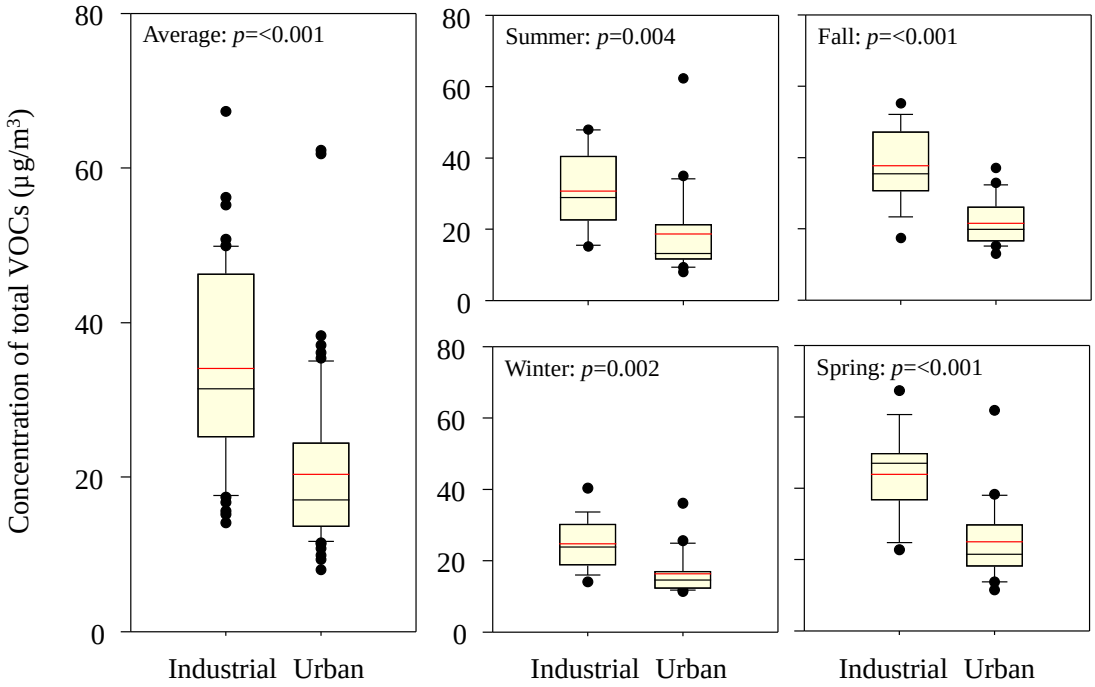

Figure 29. Comparison with concentration of total VOCs at industrial and urban site in annual average, summer, fall, winter, and spring.

3.3 Spatial distribution of VOCs

To identify spatial distribution with high resolution of VOCs, geographic information system (GIS) was used (ArcMap 10.1 software). Among various tools in GIS, Inverse Distance Weighted (IDW) was utilized to present spatial distribution of VOCs in Ulsan. IDW means that weight of each sample point (sampling site) is an inverse proportion to the distance, thus, the further distance from the point, the less the weight in helping define the un-sampled location based on equation in Figure 30 (Kea et al., 2011).

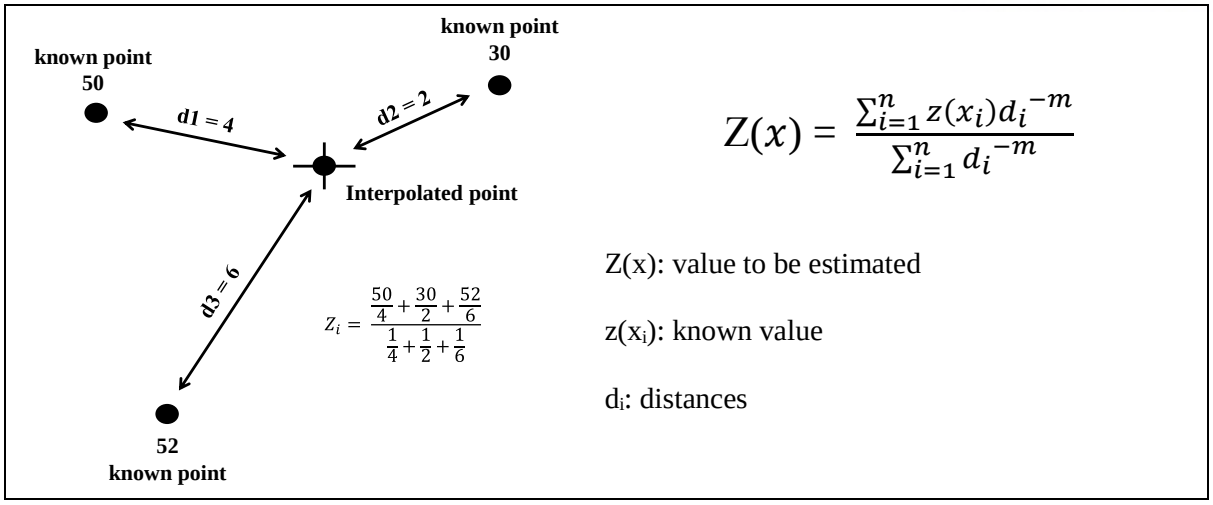

Figure 30. Procedure and equation for calculation of concentration by IDW.

As a result of analysis for spatial distribution using Arc GIS, seasonal concentration of total VOCs was high at most of industrial sites in Ulsan (Figure 31), and also wind roses at meteorological observatory were presented. The sites of U2 and I6 were classified as hot spots of VOC pollution in summer (Figure 31(a)). The reason of highest concentration at U2 would be the influence from automobile industrial complex (I1), and actual wind direction at AWS 1 located nearby I1 was northern wind in summer. It is possible to expect that VOCs emitted from I1, site nearby automobile industrial complex, moved forward U2 site, and also high concentration of total VOCs at I6 site has several potentials such as effects of petrochemical complex and museum which will be explained in source identification part.

In fall and winter, northwestern wind was dominant, thus most of VOCs emitted from industrial complex in Ulsan seem to go out forward the east sea (Figure 31(b), (c)). Unlike winter season, not only northwestern but also northeastern wind were dominant in fall. Therefore, it seemed to be that I1 and U2 sites had a less impact on other sources than winter season. Although urban sites will be less effects from industrial complexes due to wind direction in fall and winter, U2 and U3 sites located between automobile (I1), petrochemical (I6), shipbuilding and heavy (I5) industrial complexes are concerned by air quality and human health.

Overall spatial distribution of total VOCs in spring had a similar pattern with summer season (Figure 31(d)). However, unlike summer season, only I1 site was regarded as a hot spot in spring because of much higher concentration than other sites. In addition, although I5 site was classified as an industrial site and showed that emission amount of chemicals was highest in Ulsan, all of VOCs emitted from

shipbuilding and heavy industrial complex would be moved to the east sea due to southwestern wind which is obtained from AWS 2 (nearby I5 site).

In conclusion, large amount of VOCs were detected at all of industrial sites in Ulsan, except for I2 site (Figure 32). I2 site was regarded as an industrial site in this study, because the site is located directly next to petrochemical industrial complexes. Nevertheless, reasons for low concentration of total VOCs in I2 site could be an effect of northwestern wind in annual average. Also, although U2 and U3 sites were at urban area, high concentration of total VOCs were detected because these sites are located nearby automobile, shipbuilding, and heavy industrial complexes. Therefore, monitoring of VOCs at U2 and U3 sites are especially required in Ulsan.

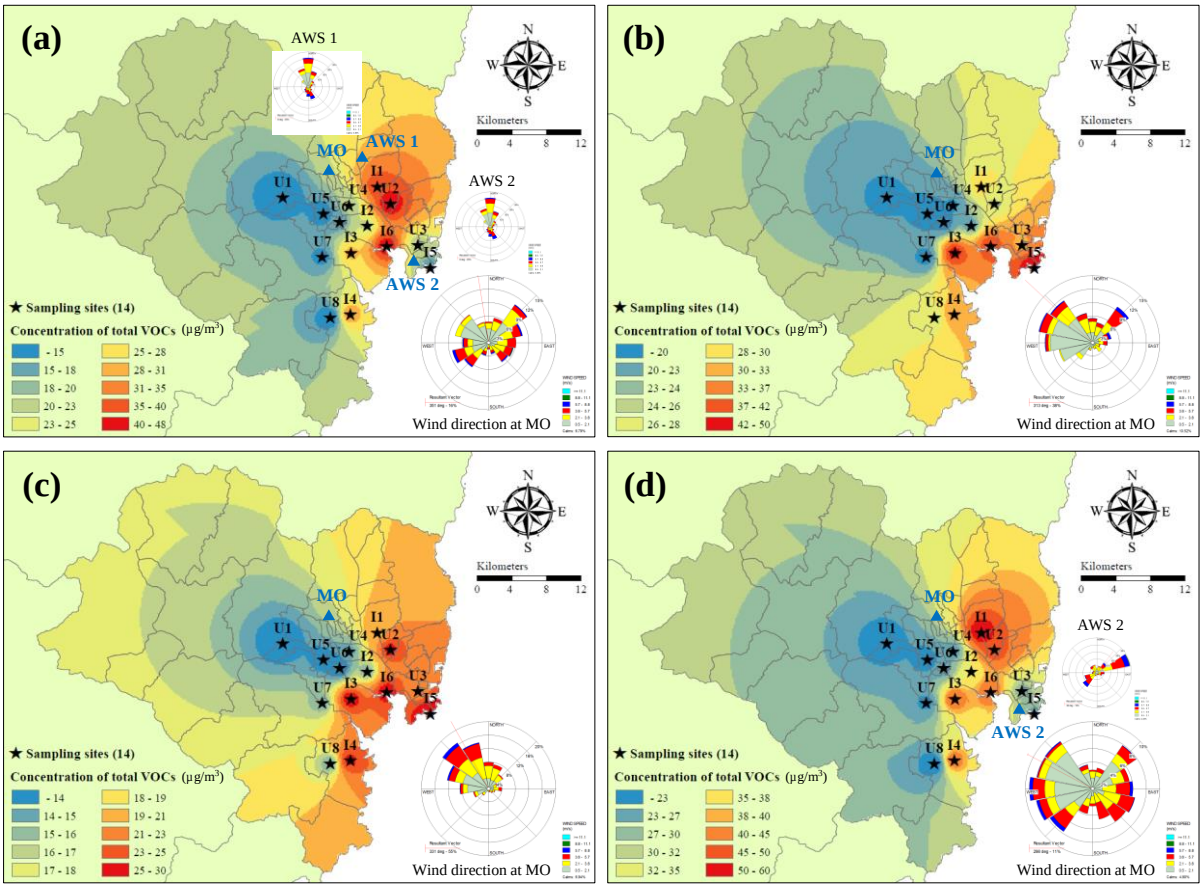

Figure 31. Spatial distributions and wind roses in (a) summer, (b) fall, (c) winter, (d) spring based on 14 sampling sites of Ulsan.

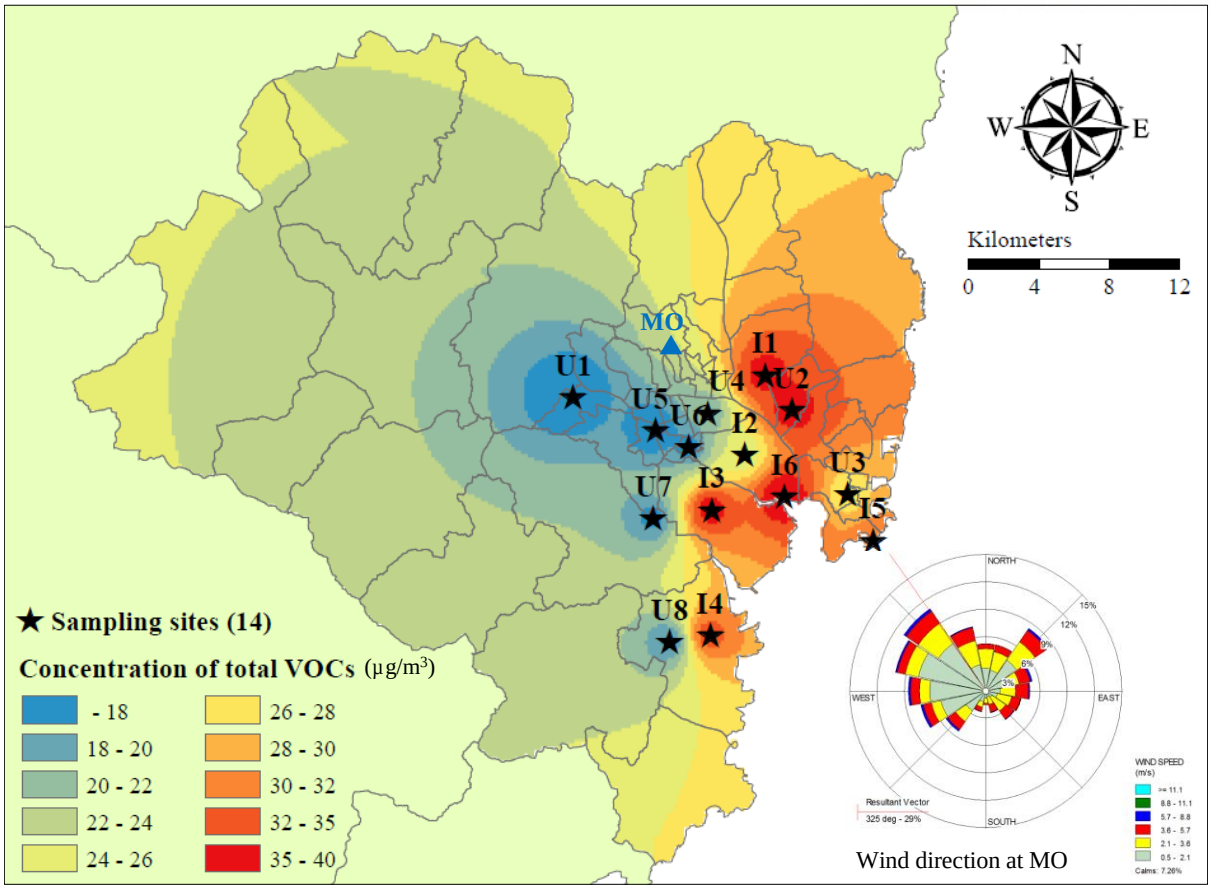

Figure 32. Spatial distributions and wind roses in annual average based on 14 sampling sites of Ulsan.

Spatial distribution of total VOCs in four seasons and annual average were explained previously, and then, measured concentration and emission amount of benzene, toluene, ethylbenzene, and m,p,o-xylene were compared using Arc GIS in Figure 33-36. Because the hot spots of two value for BTEX were quite same, the monitoring data of VOCs in this study has a reliability. Benzene was mainly emitted from non-ferrous industrial complex, and toluene was largely emitted from automobile industrial complex. In case of ethylbenzene and xylenes, main emitted source was shipbuilding and heavy industrial complexes. However, accurate amount of chemicals, emitting from industrial facilities, and the smaller point sources cannot be considered in PRTR, because boss of industrial complexes reported the emission amount of chemicals by themselves.

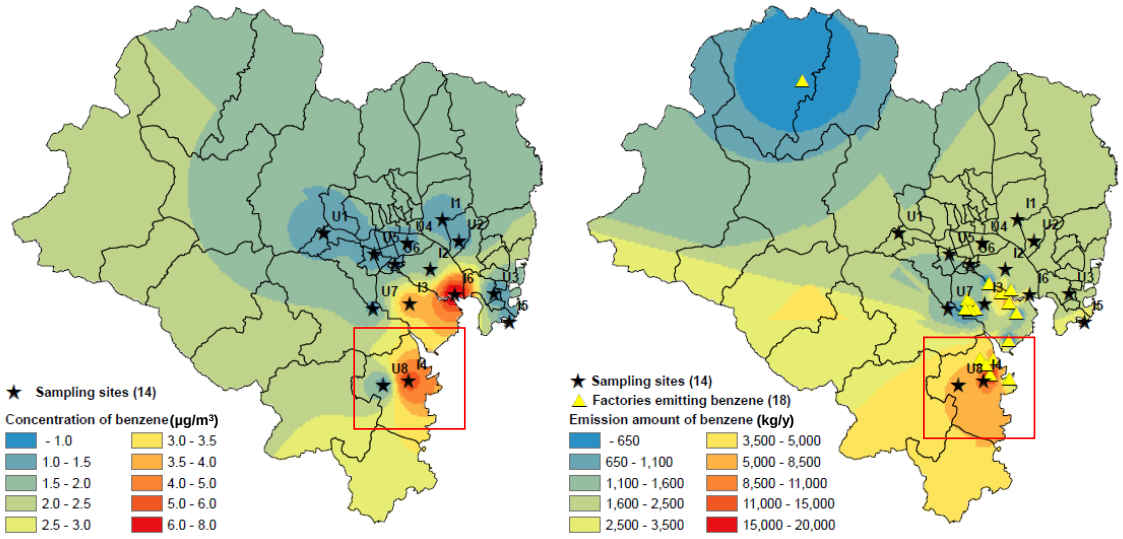

Figure 33. Comparison between measured data for benzene (left) and emission amount of benzene provided by Korea Ministry of Environment (right).

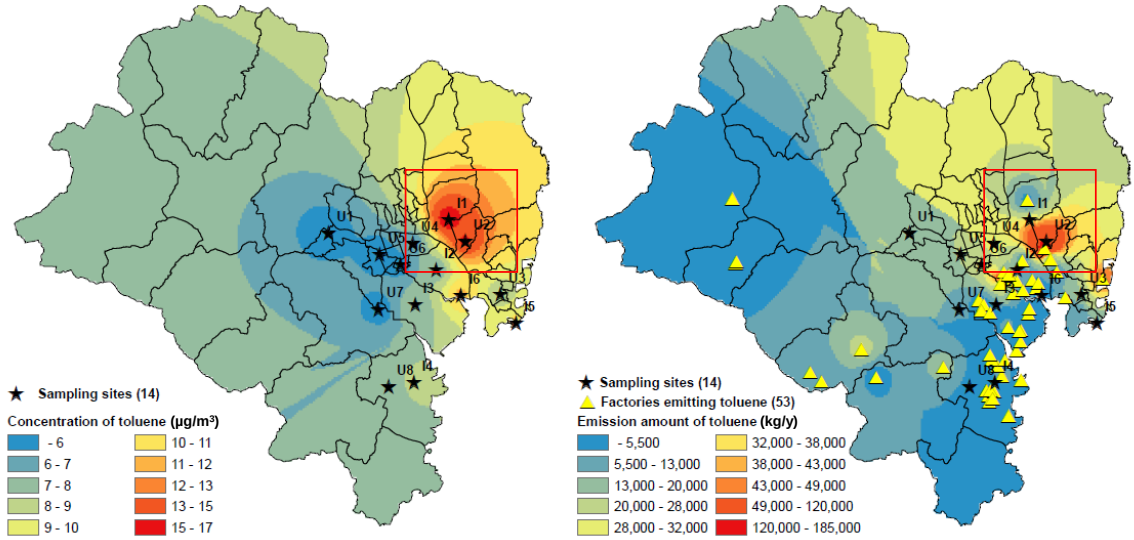

Figure 34. Comparison between measured data for toluene (left) and emission amount of toluene provided by Korea Ministry of Environment (right).

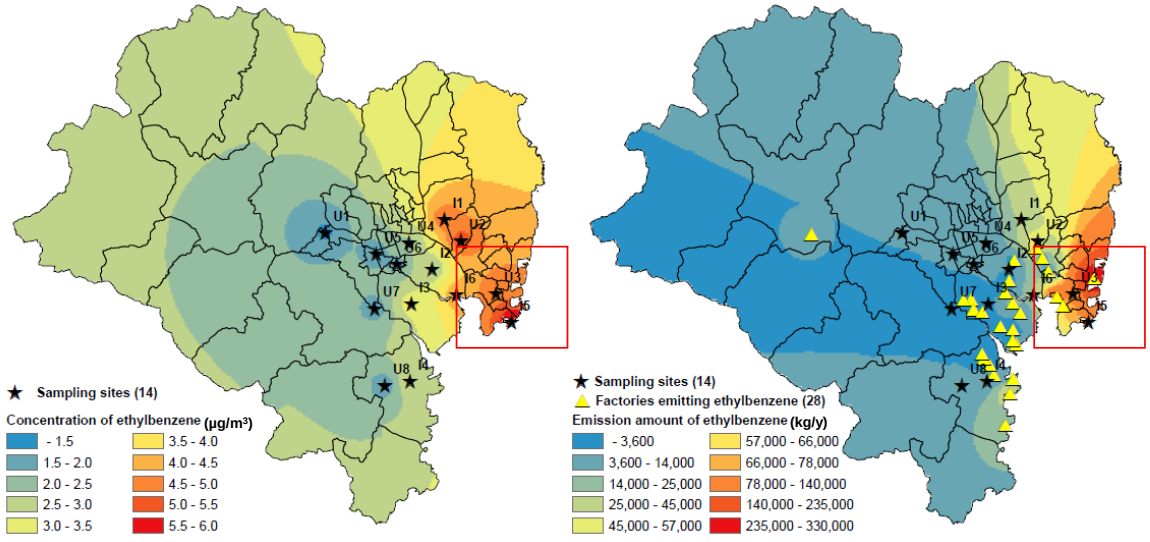

Figure 35. Comparison between measured data for ethylbenzene (left) and emission amount of ethylbenzene provided by Korea Ministry of Environment (right).

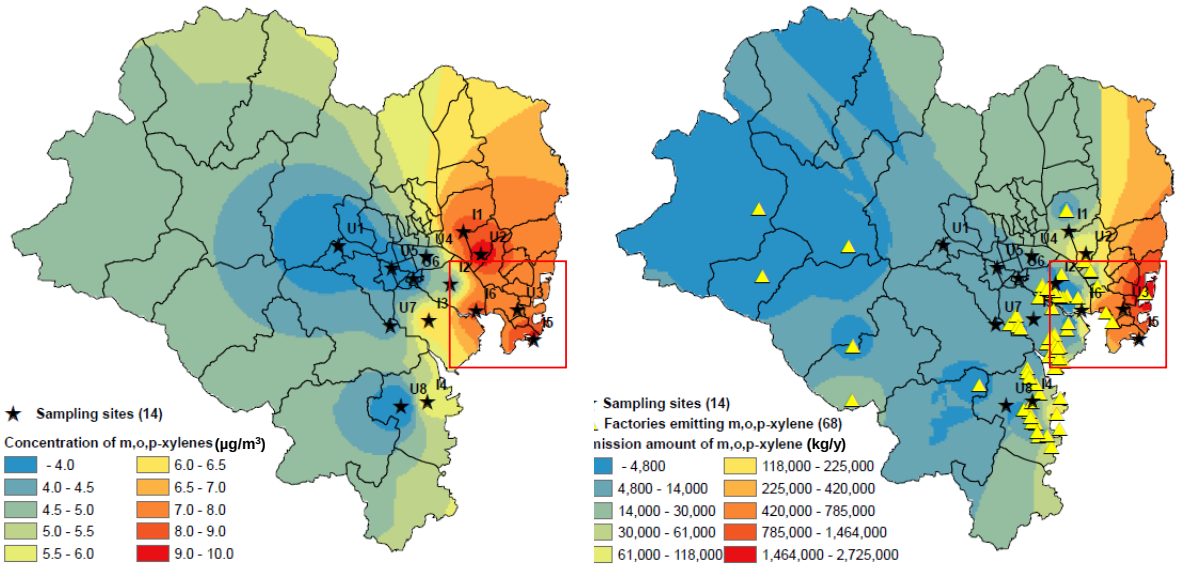

Figure 36. Comparison between measured data for m,o,p-xylene (left) and emission amount of m,o,p-xylene provided by Korea Ministry of Environment (right).

3.4 Soure identification

Two types of statistical tools including diagnostic ratios and correlation analysis were used to identify the relationship and sources of VOCs in this study.

First, Toluene/Benzene (T/B) and m,p-Xylene/Ethylbenzene (X/E) ratios were used for source identification as diagnostic ratios. Generally, T/B ratio (>4.3 or 1.5-3.0) is classified as a traffic source in previous many studies (Miller et al., 2011, Miller et al., 2012). Thus, in this study, ratio of a lower than 3.0 was selected by traffic effects. The ratio were observed by ranged from 0.8 to 23.4 (mean: 6.9, median: 5.0) in summer, from 1.7 to 12.9 (mean: 7.0, median: 5.4) in fall, from 1.2 to 6.9 (mean: 3.9, median: 3.2) in winter, from 1.0 to 18.3 (mean: 5.9, median: 4.4) in spring, and from 0.8 to 23.4 (mean: 5.9, median: 4.9) in annual average. All of the T/B ratios in this study showed a scattered distribution regardless of the seasons, except for winter season which is a little lower than other seasons (Figure 37(a)). Non-traffic sources such as paint, solvent, and metals were dominant at most of sampling sites during four seasons in Ulsan, actually, much high T/B ratio was reported in previous study (Ho et al., 2004). Among them, high T/B ratio represented at U2 and U3 site in spite of urban site, because two sites were located nearby automobile, shipbuilding, and heavy industrial complexes as mentioned above. Besides, although I3, I4, and I6 sites are industrial area, there were a few traffic effect, which was higher than non-traffic effect emitted from industrial facilities. Actually, passive air samplers were deployed next to road at I3 and I4 sites, because of this reason, it is possible to understand reason of low T/B ratio. Also, I6 site, located nearby petrochemical complex, is a whale museum which is one of the famous tourist attraction in Ulsan. Therefore, a lot of tourists who ride cars would visit there in summer and spring, which are warmer seasons than winter.

X/E ratio in this study was observed by ranged from 0.8 to 1.7 (mean: 1.0, median: 1.0) in summer, from 0.8 to 1.2 (mean: 0.9, median: 0.9) in fall, from 0.7 to 1.6 (mean: 1.0, median: 0.9) in winter, from 0.7 to 1.2 (mean: 0.9, median: 0.8) in spring, and from 0.7 to 1.7 (mean: 1.0, median: 0.9) in annual average. X/E ratio (about 1.6) showed that it was influenced by surrounding industrial facilities, and lower ratio (about 1.2) was regarded as having a more photochemical mixed VOCs (Zhang et al., 2008). The ratio in this study was a little lower or similar with other studies. Therefore, unlike other areas in Korea, Ulsan might be influenced by many kinds of industrial facilities which are located at various points (far away or closely).

In addition, spatial distributions of each diagnostic ratio (T/B and X/E) were conducted using the Arc GIS in this study (Figure S12-13). As expected, levels of T/B ratio at I1 and U2 sites (automobile industrial complex) were high in all seasons, also U3 and I5 sites showed high levels of T/B ratio in fall

and winter. On the other hand, those at non-ferrous industrial complex were quite low because usage of solvents would not be frequent. In case of X/E ratio, a variety of patterns were presented in each season.

Figure 37(b) shows ratios at industrial and urban sites except U2, U3, I3, and I4 sites in four seasons, as well as I6 site in summer and spring to identify general effects by source in Ulsan. As expected, most of urban sites in Ulsan are distributed around the 3 T/B ratio (traffic source), and although most of industrial sites were mainly effected by non-traffic source, both sources were represented at industrial sites.

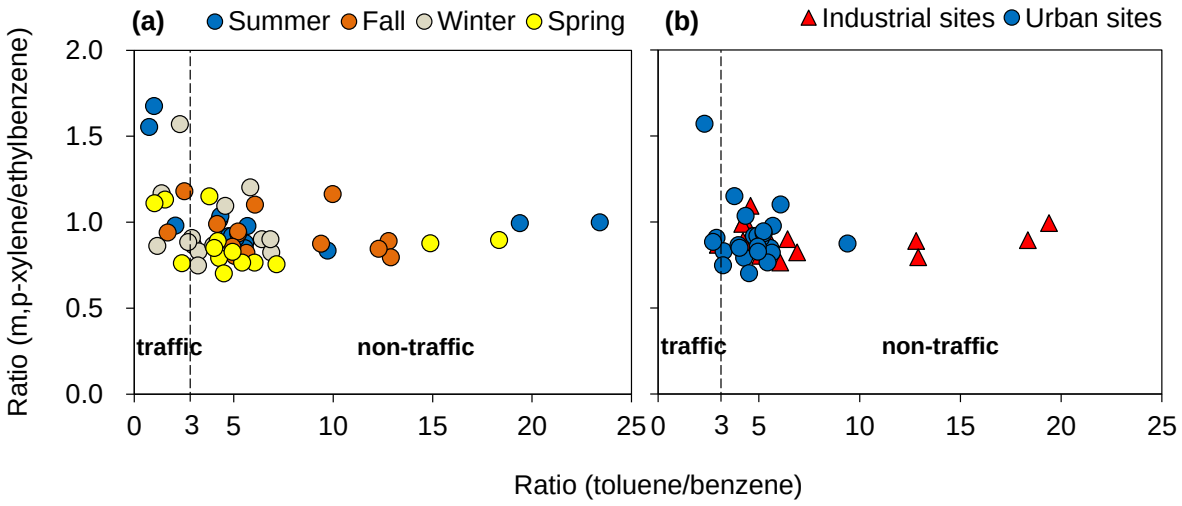

Figure 37. Toluene/benzene and m,p-xylene/ethylbenzene ratios at all of the sampling sites (a), and industrial and urban sites (removed certain sites) in four seasons (b).

Second, Pearson and Spearman correlation analysis were conducted to identify relationship with measured data and some parameters based on the four seasons and annual average (Table 10-14). Only Pearson correlation analysis, which can be applied in case of normal distribution for parameters, are shown in here, because all of the VOCs had a lognormal distribution. Among parameters, some parameters were ignored because the fraction of not detected over 50%, which parameters do not show the significant results.

As a result of correlation analysis based on the Pearson method, several parameters showed a relatively strong correlations (>0.9) between ethylbenzene and m,p-xylene, ethylbenzene and o-xylene, and o-xylene and toluene in summer, ethylbenzene and m,p-xylene, ethylbenzene and o-xylene, m,p-xylene and o-xylene, and styrene and 1,2-dichloropropane in fall, ethylbenzene and m,p-xylene, m,p-xylene and o-xylene, styrene and 1,2-dichloropropane in winter, and ethylbenzene and m,p-xylene, ethylbnezne and o-xylene, styrene and 1,2-dichloropropane in spring and annual average.

Consequently, Only ethylbenzene and m,p-xylene showed a relatively strong correlation during all of the seasons, and these two compounds were actually emitted from same sources which are shipbuilding and heavy industrial complexes in Ulsan. Except for summer season, much higher concentration of styrene and 1,2-dichloropropane were detected at I3 site in all of the seasons. These two compounds play role an indicator of products from petrochemical industrial complex (I3).

The result of good correlations (0.8-0.9) was represented between benzene and tetrachloroethylene, ethylbenzene and toluene, m,p-xylene and o-xylene, and styrene and 1,2-dichloropropane in summer, benzene and 1,1,2-trichloroethane, ethylbenzene and toluene, m,p-xylene toluene, o-xylene and toluene, and cis-1,2-dichloroethylene and trichloroethylene in fall, ethylbenzene and o-xylene, and 1,1,2-trichloroethane and 1,2-dichloropropane in winter, and SO_2 and chloroform, ethylbenzene and toluene, m,p-xylene and o-xylene, m,p-xylene and toluene, o-xylene and toluene, chloroform and trichloroethylene, and cis-1,2-dichloroethylene and trichloroethylene in spring and annual average.

In this study, there is no good correlations with target compounds in all of four seasons, however, benzene and tetrachloroethylene in summer had a good correlation, indicating a marker of industrial emissions in previous study (Zhang et al., 2015). In addition, cis-1,2-dichloroethylene and trichloroethylene in fall, spring, and annual average showed a good correlation. High concentration of these two compounds were actually detected at I4 site in comparison with other sampling sites, therefore, it could be influenced by non-ferrous industrial complex (I4). Also, SO_2 and chloroform in spring and annual average might have the same emission sources.

The result of moderate correlations (0.6-0.8) were related with a variety of compounds, however, there were no certain characteristics which would be due to many kinds of parameters (the number of parameter in summer: 21, fall: 24, winter: 23, and spring: 27). Lastly, result of the negative correlations (<-0.5) were showed between O_3 and NO_2 in fall, winter, spring, and annual average, and vinyl chloride and ethylbenzene, vinyl chloride and m,p-xylene, and vinyl chloride and o-xylene. As mentioned previously, O_3 is actually produced through reaction with NO_2 and VOCs in the presence of sunlight, therefore, O_3 and NO_2 are related inversely. Also, vinyl chloride, ethylbenzene, m,p-xylene, and o-xylene in only spring had a negative correlation. Ethylbenzene, m,p-xylene, and o-xylene emitted mainly from shipbuilding and heavy industrial complexes in Ulsan might be effected by sources of vinyl chloride. Actually, concentration of ethylbenzene, m,p-xylene, and o-xylene were highest in spring.

It is concluded that the relationship of each compound can be explained as similar emission sources based on Pearson correlation analysis in four seasons and annual average.

Table 10. Correlation analysis of criteria air pollutants and 16 VOCs, which remove upper 50% not detected target compounds (28 VOCs) in summer.

Pearson	SO_2	CO	O_3	NO_2	PM_{10}	BZ	EB	m,p-X	o-X	SR	TU	1,1,2-TCA	1,2-DCA	1,2-DCP	BMF	CTC	CF	cis-1,2-DCE	TeCE	TriCE	MTBE
SO_2	1																				
CO	0.570**	1																			
O_3	-0.052	0.446*	1																		
NO_2	0.007	-0.318	-0.197	1																	
PM_{10}	0.242	-0.012	-0.037	0.551**	1																
BZ	0.477*	0.300	0.107	0.090	-0.004	1															
EB	0.262	0.012	-0.133	0.319	0.697**	0.148	1														
m,p-X	0.445*	0.078	-0.107	0.322	0.635**	0.461*	0.914**	1													
o-X	0.251	-0.106	-0.178	0.346	0.663**	0.160	0.970**	0.888**	1												
SR	0.194	0.148	0.121	0.209	0.136	0.146	0.099	0.096	0.171	1											
TU	0.191	-0.353	-0.330	0.420*	0.608**	0.143	0.853**	0.797**	0.915**	0.041	1										
1,1,2-TCA	0.755**	0.266	-0.038	0.119	0.234	0.710**	0.324	0.587**	0.354	0.256	0.362	1									
1,2-DCA	0.467*	0.372	0.330	0.115	0.089	0.590**	-0.003	0.169	0.061	0.346	0.034	0.525**	1								
1,2-DCP	0.143	0.025	0.025	0.196	0.075	0.053	0.105	0.071	0.200	0.806**	0.147	0.223	0.302	1							
BMF	0.028	0.306	0.156	0.008	0.188	0.351	0.276	0.366	0.181	-0.06	0.016	0.035	-0.125	-0.203	1						
CTC	0.092	-0.077	-0.045	0.06	-0.155	-0.228	-0.119	-0.153	-0.029	-0.111	0.099	0.001	0.320	0.132	-0.376	1					
CF	0.590**	0.333	0.156	0.083	0.042	0.307	0.03	0.147	0.055	0.049	0.094	0.567**	0.750**	0.111	-0.293	0.593**	1				
cis-1,2-DCE	0.688**	0.015	-0.308	0.254	0.308	0.359	0.257	0.511*	0.267	-0.152	0.357	0.787**	0.230	-0.112	-0.221	0.164	0.530*	1			
TeCE	0.315	0.262	0.090	0.016	-0.028	0.818**	0.168	0.362	0.199	-0.004	0.228	0.440*	0.683**	-0.046	0.236	0.064	0.371	0.108	1		
TriCE	0.701**	0.308	-0.115	-0.140	-0.097	0.496**	-0.093	0.156	-0.081	0.002	-0.004	0.799**	0.426*	-0.009	-0.234	0.108	0.622**	0.742**	0.320	1	
MTBE	0.440*	0.363	0.014	-0.112	0.022	-0.096	0.065	0.043	0.076	-0.068	0.020	0.235	0.455*	-0.050	-0.289	0.708**	0.780**	0.292	0.089	0.330	1

**Correlation is significant at the 0.01 level (2-tailed) and *Correlation is significant at the 0.05 level (1-tailed)

>0.9 0.8-0.9 0.6-0.8 <-0.5

BZ: Benzene, EB: Ethylbenzene, m,p-X: m,p-Xylene, o-X: o-Xylene, SR: Styrene, TU: Toluene, 1,1,1-TCA: 1,1,1-Trichloroethane, 1,1,2-TCA: 1,1,2-Trichloroethane, 1,2,4-TCB: 1,2,4-Trichlorobenzene, 1,2-DCB: 1,2-Dichlorobenzene, 1,2-DCA: 1,2-Dichloroethane, 1,2-DCP: 1,2-Dichloropropane, 1,4-DCB: 1,4-Dichlorobenzene, BMF, Bromoform, CTC: Carbon tetrachloride, CF: Chloroform, cis-1,2-DCE: cis-1,2-Dichloroethylene, DCM: Dichloromethane, TeCE: Tetrachloroethylene, TriCE: Trichloroethylene, VC: Vinyl chloride, and MTBE: Methyl tert-butyl ether

Table 11. Correlation analysis of criteria air pollutants and 16 VOCs, which remove upper 50% not detected target compounds (28 VOCs) in fall.

Pearson	SO_2	CO	O_3	NO_2	PM_{10}	BZ	EB	m,p-X	o-X	SR	TU	1,1,1-TCA	1,1,2-TCA	1,2-DCA	1,2-DCP	BMF	CTC	CF	cis-1,2-DCE	DCM	TeCE	TriCE	VC	MTBE
SO_2	1																							
CO	0.073	1																						
O_3	0.421*	0.046	1																					
NO_2	-0.325	0.114	-0.756**	1																				
PM_{10}	0.013	0.719**	-0.203	0.297	1																			
BZ	0.639**	-0.011	0.049	-0.063	-0.116	1																		
EB	0.148	0.112	0.560**	-0.551**	-0.073	0.111	1																	
m,p-X	0.192	0.098	0.542**	-0.539**	-0.060	0.213	0.968**	1																
o-X	0.125	0.094	0.525**	-0.504**	-0.086	0.239	0.939**	0.947**	1															
SR	0.180	0.120	-0.076	0.113	-0.050	0.698**	0.058	0.072	0.294	1														
TU	0.116	-0.066	0.383*	-0.476*	-0.072	0.159	0.849**	0.878**	0.835**	-0.028	1													
1,1,1-TCA	-0.294	-0.199	-0.110	-0.118	-0.052	-0.031	-0.012	-0.005	0.031	0.013	0.135	1												
1,1,2-TCA	0.479**	0.059	0.067	-0.110	0.052	0.831**	0.183	0.256	0.348	0.766**	0.245	0.153	1											
1,2-DCA	0.262	0.161	-0.186	0.189	-0.076	0.715**	0.040	0.104	0.206	0.774**	-0.004	0.003	0.711**	1										
1,2-DCP	0.041	0.142	-0.172	0.178	0.067	0.634**	0.083	0.124	0.325	0.943**	0.073	0.051	0.745**	0.731**	1									
BMF	0.304	0.024	0.490*	-0.386	-0.205	0.252	0.749**	0.745**	0.779**	0.142	0.787**	-0.094	0.226	0.173	0.092	1								
CTC	0.109	-0.134	0.151	-0.094	-0.190	0.188	0.245	0.192	0.315	0.207	0.316	0.350	0.300	0.212	0.124	0.533**	1							
CF	0.628**	-0.004	0.082	-0.111	0.067	0.573**	0.086	0.158	0.045	0.07	0.169	-0.045	0.427*	0.372	0.033	0.233	0.209	1						
cis-1,2-DCE	0.665**	-0.185	0.281	-0.406*	-0.156	0.579**	0.349	0.457*	0.328	0.025	0.549**	-0.039	0.493**	0.192	0.030	0.430*	0.107	0.587**	1					
DCM	0.306	0.01	-0.202	0.218	0.243	0.178	-0.253	-0.247	-0.296	-0.155	-0.167	-0.233	0.082	-0.102	-0.222	0.066	0.264	0.329	0.116	1				
TeCE	0.264	0.071	-0.004	0.039	-0.078	0.410*	0.277	0.369	0.235	-0.020	0.374*	-0.070	0.090	0.427*	0.002	0.397*	0.147	0.568**	0.365	-0.002	1			
TriCE	0.539**	-0.317	-0.025	-0.18	-0.234	0.556**	0.042	0.127	0.028	0.003	0.352	0.032	0.407*	0.226	-0.028	0.288	0.294	0.652**	0.805**	0.230	0.469*	1		
VC	0.274	0.012	0.092	-0.044	-0.080	0.269	-0.227	-0.208	-0.124	0.376*	-0.353	0.123	0.438*	0.407*	0.245	-0.275	-0.053	0.180	0.022	-0.049	-0.253	-0.012	1	
MTBE	0.015	0.078	0.258	-0.385*	0.267	-0.378*	-0.025	-0.100	-0.028	-0.259	-0.006	0.315	-0.214	-0.442*	-0.312	-0.040	0.225	-0.195	-0.200	-0.079	-0.358	-0.137	0.056	1

**Correlation is significant at the 0.01 level (2-tailed) and *Correlation is significant at the 0.05 level (1-tailed)

>0.9 0.8-0.9 0.6-0.8 <-0.5

BZ: Benzene, EB: Ethylbenzene, m,p-X: m,p-Xylene, o-X: o-Xylene, SR: Styrene, TU: Toluene, 1,1,1-TCA: 1,1,1-Trichloroethane, 1,1,2-TCA: 1,1,2-Trichloroethane, 1,2,4-TCB: 1,2,4-Trichlorobenzene, 1,2-DCB: 1,2-Dichlorobenzene, 1,2-DCA: 1,2-Dichloroethane, 1,2-DCP: 1,2-Dichloropropane, 1,4-DCB: 1,4-Dichlorobenzene, BMF, Bromoform, CTC: Carbon tetrachloride, CF: Chloroform, cis-1,2-DCE: cis-1,2-Dichloroethylene, DCM: Dichloromethane, TeCE: Tetrachloroethylene, TriCE: Trichloroethylene, VC: Vinyl chloride, and MTBE: Methyl tert-butyl ether

Table 12. Correlation analysis of criteria air pollutants and 16 VOCs, which remove upper 50% not detected target compounds (28 VOCs) in winter.

Pearson	SO_2	CO	O_3	NO_2	PM_{10}	BZ	EB	m,p-X	o-X	SR	TU	1,1,1-TCA	1,1,2-TCA	1,2-DCP	1,4-DCB	CTC	CF	cis-1,2-DCE	DCM	TeCE	TriCE	VC	MTBE
SO_2	1																						
CO	-0.200	1																					
O_3	0.455*	-0.329	1																				
NO_2	-0.463*	0.082	-0.626**	1																			
PM_{10}	-0.205	-0.190	0.329	-0.03	1																		
BZ	0.657**	-0.386*	0.270	-0.336	0.124	1																	
EB	-0.062	0.051	0.200	-0.261	-0.240	-0.027	1																
m,p-X	-0.117	-0.04	0.145	-0.292	-0.173	0.047	0.939**	1															
o-X	-0.140	-0.079	0.143	-0.217	-0.062	0.097	0.883**	0.951**	1														
SR	0.322	-0.223	-0.05	0.125	-0.046	0.517**	0.015	-0.011	0.201	1													
TU	-0.09	-0.049	0.021	-0.097	-0.062	0.036	0.787**	0.784**	0.736**	-0.065	1												
1,1,1-TCA	-0.023	0.005	0.204	-0.206	0.177	0.206	0.308	0.265	0.296	0.026	0.234	1											
1,1,2-TCA	0.390*	-0.168	-0.012	0.039	-0.123	0.724**	0.023	-0.015	0.117	0.773**	0.036	0.203	1										
1,2-DCP	0.623**	-0.373	0.066	-0.081	-0.062	0.559**	0.036	0.117	0.131	0.463*	0.272	-0.119	0.375*	1									
1,4-DCB	0.121	-0.213	-0.146	0.196	0.042	0.491**	0.069	0.079	0.309	0.912**	0.110	0.030	0.805**	0.371	1								
CTC	0.274	-0.157	0.188	0.045	0.336	0.346	0.053	0.095	0.190	0.094	0.308	0.358	0.242	0.422*	0.187	1							
CF	0.742**	-0.221	0.249	-0.358	0.09	0.775**	-0.032	0.06	-0.01	0.136	0.173	0.009	0.313	0.748**	0.066	0.393*	1						
cis-1,2-DCE	0.340	-0.287	0.229	-0.386*	0.07	0.495**	0.432*	0.497**	0.486**	0.03	0.703**	0.182	0.224	0.417*	0.159	0.448*	0.556**	1					
DCM	0.270	-0.066	0.124	-0.431*	0.259	0.559**	0.15	0.285	0.187	-0.167	0.421*	0.153	0.127	0.360	-0.089	0.273	0.731**	0.681**	1				
TeCE	0.311	-0.199	-0.076	0.097	-0.133	0.076	0.094	0.163	0.069	-0.014	0.384*	-0.256	-0.084	0.793**	-0.038	0.328	0.525**	0.250	0.207	1			
TriCE	0.469*	-0.367	0.092	-0.233	0.027	0.546**	0.000	0.082	0.006	-0.023	0.417*	0.116	0.213	0.612**	-0.006	0.404*	0.738**	0.774**	0.711**	0.480**	1		
VC	0.072	0.281	-0.039	-0.104	0.021	-0.003	0.231	0.162	0.257	0.14	0.141	0.131	0.012	-0.092	0.176	0.214	-0.036	0.156	-0.046	-0.216	-0.188	1	
MTBE	-0.09	0.547**	-0.193	-0.299	-0.083	-0.142	0.040	0.037	0.014	-0.300	0.012	0.055	-0.213	-0.367	-0.242	-0.014	-0.093	0.216	0.192	-0.377*	0.033	0.519**	1

**Correlation is significant at the 0.01 level (2-tailed) and *Correlation is significant at the 0.05 level (1-tailed)

>0.9 0.8-0.9 0.6-0.8 <-0.5

BZ: Benzene, EB: Ethylbenzene, m,p-X: m,p-Xylene, o-X: o-Xylene, SR: Styrene, TU: Toluene, 1,1,1-TCA: 1,1,1-Trichloroethane, 1,1,2-TCA: 1,1,2-Trichloroethane, 1,2,4-TCB: 1,2,4-Trichlorobenzene, 1,2-DCB: 1,2-Dichlorobenzene, 1,2-DCA: 1,2-Dichloroethane, 1,2-DCP: 1,2-Dichloropropane, 1,4-DCB: 1,4-Dichlorobenzene, BMF, Bromoform, CTC: Carbon tetrachloride, CF: Chloroform, cis-1,2-DCE: cis-1,2-Dichloroethylene, DCM: Dichloromethane, TeCE: Tetrachloroethylene, TriCE: Trichloroethylene, VC: Vinyl chloride, and MTBE: Methyl tert-butyl ether

Table 13. Correlation analysis of criteria air pollutants and 16 VOCs, which remove upper 50% not detected target compounds (28 VOCs) in spring.

Pearson	SO_2	CO	O_3	NO_2	PM_{10}	BZ	EB	m,p-X	o-X	SR	TU	1,1,2-TCA	1,2-DCA	1,2-DCP	BMF	CTC	CF	cis-1,2-DCE	TeCE	TriCE	VC	MTBE
SO_2	1																					
CO	0.383*	1																				
O_3	0.306	0.128	1																			
NO_2	-0.045	0.475*	-0.522**	1																		
PM_{10}	0.624**	0.094	-0.082	0.019	1																	
BZ	0.449*	0.359	0.235	0.173	0.258	1																
EB	0.181	0.137	0.023	0.224	0.357	0.218	1															
m,p-X	0.245	0.107	-0.014	0.216	0.439*	0.393*	0.962**	1														
o-X	0.12	0.123	-0.061	0.275	0.372	0.147	0.925**	0.893**	1													
SR	0.129	0.403*	0.046	0.295	0.060	0.188	0.097	0.028	0.322	1												
TU	0.095	-0.064	-0.353	0.374	0.424*	0.094	0.841**	0.846**	0.842**	0.037	1											
1,1,2-TCA	0.705**	0.118	0.235	-0.010	0.544**	0.769**	0.424*	0.581**	0.340	0.015	0.388*	1										
1,2-DCA	0.420*	0.354	0.204	0.241	0.309	0.403*	-0.12	-0.062	-0.031	0.404*	-0.097	0.272	1									
1,2-DCP	0.109	0.308	-0.036	0.330	0.107	0.140	0.206	0.128	0.431*	0.978**	0.200	0.049	0.329	1								
BMF	0.041	0.463*	0.333	0.060	-0.198	0.508*	0.173	0.25	0.053	-0.014	-0.068	0.294	0.014	-0.097	1							
CTC	0.251	0.04	0.092	0.145	0.028	-0.173	0.101	0.072	0.104	-0.232	0.177	0.122	0.282	-0.189	-0.238	1						
CF	0.836**	0.09	0.132	-0.163	0.506**	0.257	-0.034	0.06	-0.071	-0.088	0.002	0.626**	0.277	-0.093	-0.182	0.447*						
cis-1,2-DCE	0.588**	-0.266	0.099	-0.134	0.472*	0.262	0.314	0.401*	0.278	-0.076	0.426*	0.749**	0.162	0.017	-0.279	0.368	0.705**	1				
TeCE	0.500**	0.385*	0.086	0.166	0.368	0.708**	0.278	0.416*	0.164	-0.104	0.263	0.596**	0.490**	-0.125	0.318	0.227	0.354	0.246	1			
TriCE	0.673**	-0.164	0.226	-0.287	0.455*	0.419*	-0.064	0.072	-0.114	-0.071	-0.003	0.752**	0.229	-0.058	-0.142	0.131	0.804**	0.848**	0.251	1		
VC	-0.058	0.108	-0.294	-0.067	0.100	-0.29	-0.544**	-0.558**	-0.561**	-0.123	-0.444*	-0.475*	0.023	-0.194	-0.391	-0.295	-0.074	-0.455*	-0.137	-0.186	1	
MTBE	0.325	0.300	0.012	0.034	0.243	0.244	0.098	0.183	0.032	-0.257	0.097	0.177	0.292	-0.286	0.005	0.273	0.29	0.139	0.690**	0.146	0.143	1

**Correlation is significant at the 0.01 level (2-tailed) and *Correlation is significant at the 0.05 level (1-tailed)

>0.9 0.8-0.9 0.6-0.8 <-0.5

BZ: Benzene, EB: Ethylbenzene, m,p-X: m,p-Xylene, o-X: o-Xylene, SR: Styrene, TU: Toluene, 1,1,1-TCA: 1,1,1-Trichloroethane, 1,1,2-TCA: 1,1,2-Trichloroethane, 1,2,4-TCB: 1,2,4-Trichlorobenzene, 1,2-DCB: 1,2-Dichlorobenzene, 1,2-DCA: 1,2-Dichloroethane, 1,2-DCP: 1,2-Dichloropropane, 1,4-DCB: 1,4-Dichlorobenzene, BMF, Bromoform, CTC: Carbon tetrachloride, CF: Chloroform, cis-1,2-DCE: cis-1,2-Dichloroethylene, DCM: Dichloromethane, TeCE: Tetrachloroethylene, TriCE: Trichloroethylene, VC: Vinyl chloride, and MTBE: Methyl tert-butyl ether

Table 14. Correlation analysis of criteria air pollutants and 16 VOCs, which remove upper 50% not detected target compounds (28 VOCs) in annual average.

Pearson	SO_2	CO	O_3	NO_2	PM_{10}	BZ	EB	m,p-X	o-X	SR	TU	1,1,1-TCA	1,1,2-TCA	1,2,4-TCB	1,2-DCB	1,2-DCA	1,2-DCP	1,4-DCB	BMF	CTC	CF	cis-1,2-DCE	DCM	TeCE	TriCE	VC	MTBE
SO_2	1																										
CO	0.400*	1																									
O_3	0.344	0.148	1																								
NO_2	-0.315	0.020	-0.690**	1																							
PM_{10}	0.216	0.137	-0.384*	0.298	1																						
BZ	0.631**	0.072	0.106	0.017	0.055	1																					
EB	0.062	0.216	0.207	-0.171	0.379*	0.105	1																				
m,p-X	0.209	0.138	0.120	-0.146	0.447*	0.350	0.939**	1																			
o-X	0.022	0.155	0.050	-0.062	0.436*	0.113	0.934**	0.895**	1																		
SR	0.184	0.132	-0.038	0.211	-0.029	0.300	0.047	0.013	0.279	1																	
TU	0.013	0.016	-0.286	0.144	0.628**	0.132	0.810**	0.848**	0.810**	-0.029	1																
1,1,1-TCA	-0.222	-0.174	-0.166	-0.131	-0.06	-0.109	0.082	0.129	0.186	-0.060	0.109	1															
1,1,2-TCA	0.733**	0.104	0.058	-0.024	0.277	0.726**	0.198	0.354	0.301	0.594**	0.287	-0.094	1														
1,2,4-TCB	-0.128	-0.054	-0.489*	0.407	0.626**	-0.045	0.441	0.426	0.484*	0.174	0.736**	0.149	0.310	1													
1,2-DCB	-0.24	-0.151	-0.175	-0.210	-0.32	-0.059	-0.199	-0.179	-0.219	-0.150	-0.101	0.02	-0.321	-0.181	1												
1,2-DCA	0.464*	0.172	0.043	0.218	0.028	0.766**	-0.010	0.141	0.138	0.710**	-0.037	-0.127	0.670**	0.027	-0.042	1											
1,2-DCP	0.123	0.069	-0.157	0.277	0.115	0.248	0.148	0.118	0.404*	0.967**	0.155	-0.018	0.600**	0.322	-0.167	0.652**	1										
1,4-DCB	-0.095	0.020	-0.285	0.194	0.105	0.146	0.171	0.243	0.167	-0.029	0.38	-0.021	0.046	0.344	0.779**	0.187	0.012	1									
BMF	0.075	0.219	0.377*	-0.228	-0.096	0.355	0.636**	0.627**	0.483**	-0.11	0.359	0.045	0.044	0.069	0.112	0.144	-0.141	0.340	1								
CTC	0.152	0.464*	-0.119	0.216	0.194	-0.089	-0.227	-0.212	-0.183	-0.09	-0.130	0.110	-0.032	-0.06	-0.301	0.041	-0.084	-0.14	-0.094	1							
CF	0.894**	0.226	0.183	-0.283	0.252	0.591**	-0.09	0.116	-0.135	-0.024	-0.022	-0.132	0.653**	-0.173	-0.24	0.304	-0.069	-0.103	-0.032	0.271	1						
cis-1,2-DCE	0.638**	-0.133	0.191	-0.312	0.25	0.447*	0.246	0.412*	0.193	-0.091	0.334	-0.006	0.586**	0.004	-0.114	0.133	-0.043	0.055	0.158	0.094	0.713**	1					
DCM	0.552**	0.035	-0.187	-0.04	0.465*	0.366	0.085	0.273	0.046	-0.221	0.294	0.002	0.475*	0.175	-0.288	-0.009	-0.175	-0.070	-0.023	0.170	0.723**	0.619**	1				
TeCE	0.316	0.182	-0.007	0.111	0.034	0.786**	0.193	0.413*	0.113	-0.037	0.225	-0.090	0.270	0.025	0.214	0.568**	-0.079	0.471*	0.549**	-0.042	0.278	0.167	0.137	1			
TriCE	0.764**	-0.139	0.106	-0.278	0.109	0.611**	-0.163	0.072	-0.204	-0.047	0.015	-0.090	0.667**	-0.109	0.016	0.273	-0.064	0.028	-0.073	0.052	0.889**	0.824**	0.697**	0.264	1		
VC	0.271	0.369	0.203	-0.170	0.06	-0.105	0.062	0.001	0.113	0.157	-0.114	0.004	0.082	-0.09	-0.178	0.104	0.116	-0.16	0.048	0.195	0.058	0.002	0.007	-0.171	-0.073	1	
MTBE	0.349	0.532**	-0.027	-0.259	0.232	-0.194	-0.053	-0.027	-0.083	-0.289	-0.03	0.149	-0.136	0.011	0.122	-0.164	-0.315	0.158	-0.102	0.401*	0.277	0.073	0.168	0.018	0.085	0.400*	1

**Correlation is significant at the 0.01 level (2-tailed) and *Correlation is significant at the 0.05 level (1-tailed)

>0.9 0.8-0.9 0.6-0.8 <-0.5

BZ: Benzene, EB: Ethylbenzene, m,p-X: m,p-Xylene, o-X: o-Xylene, SR: Styrene, TU: Toluene, 1,1,1-TCA: 1,1,1-Trichloroethane, 1,1,2-TCA: 1,1,2-Trichloroethane, 1,2,4-TCB: 1,2,4-Trichlorobenzene, 1,2-DCB: 1,2-Dichlorobenzene, 1,2-DCA: 1,2-Dichloroethane, 1,2-DCP: 1,2-Dichloropropane, 1,4-DCB: 1,4-Dichlorobenzene, BMF, Bromoform, CTC: Carbon tetrachloride, CF: Chloroform, cis-1,2-DCE: cis-1,2-Dichloroethylene, DCM: Dichloromethane, TeCE: Tetrachloroethylene, TriCE: Trichloroethylene, VC: Vinyl chloride, and MTBE: Methyl tert-butyl ether

3.5 Risk assessment

Ulsan, known as one of the heavy industrial city in South, Korea has many kinds of VOC sources, therefore, a lot of people living and working in Ulsan can be exposed to high concentration of VOCs, and risk assessment for VOCs are really required. Based on the measured concentrations and some data including inhalation rate, exposure duration, body weight and so on, risk assessment was conducted for benzene by carcinogenic risk, toluene, ethylbenzene, and xylenes by non-carcinogenic risk in this study. Actually, the BTEX accounted for most of measured VOCs in four seasons.

To assess risk of BTEX using Monte Carlo simulation, some parameters were used as follows: concentration of BTEX (C): measured value $\mu g/m^3$ (normal distribution), inhalation rate (IR): 13 m^3/day (normal distribution), exposure duration (ED): 25 year (point), exposure frequency (EF): 345 event/year (triangular distribution), body weight (BT): 62 kg (normal distribution), and average time (AT): 70 year (point). As a carcinogenic compounds, risk of benzene ranged between -2.E-05-4.E-05 in summer, -3.E-06-1.E-05 in fall, -4.E-06-9.E-06 in winter, and -9.E-06-2.E-05 in spring (Figure 36a). Carcinogenic risk of benzene was highest in summer, followed by spring, fall and winter. Also, risk at percentiles ranging 80-100% in summer and 100% in fall and spring was higher than acceptable levels at 1.E-06 (US EPA) and 1.E-05 (WHO). It can expect that carcinogenic risk of benzene may reach high levels in the worst case, such as hazardous chemical accidents.

On the other hand, toluene, ethylbenzene, and m,p,o-xylene ranged between -5.E-0.4-1.E-03, -6.E-04-3.E-03, and -1.E-02-5.E-02 in summer, -7.E-05-1.E-03, -1.E-03-3.E-03, and -1.E-02-4.E-02 in fall, -4.E-05-9.E-04, -4.E-04-2.E-03, and -7.E-03-4.E-02 in winter, and -5.E-04-2.E-03, -4.E-04-4.E-03, and -1.E-02-7.E-02 in spring, respectively (Figure 36b-d). Risk of TEX was not exceed the standard acceptable HQ given by US EPA. Although concentration of TEX was higher than other target compounds during all of the sampling periods in this study, there was no cancer risk for human health because of having low carcinogenicity as a non-carcinogenic compounds.

In addition, risk assessment of 1,2-dichloroethane, vinyl chloride, 1,3-butadiene (carcinogenic compounds), and MTBE (non-carcinogenic compound) were conducted (Figure S11). Except for 1,2-dichloroethane, three compounds did not have cancer risk for human health (< 1.E-06 or 1 > HQ). Although concentration of 1,2-dichloroethane was much lower than those of TEX, risk was higher than acceptable levels at percentiles ranging 100% in summer, 70-100% in fall, 100% in winter and spring. It show that carcinogenic compounds of low concentration should be conducted for risk assessment.

However, as the uppermost limit, exceeding or non-exceeding acceptable levels is not important, because it is only the predicted values in this study. Therefore, the results in this study can be utilized to make a limit value of air pollutants or manage clean air act.

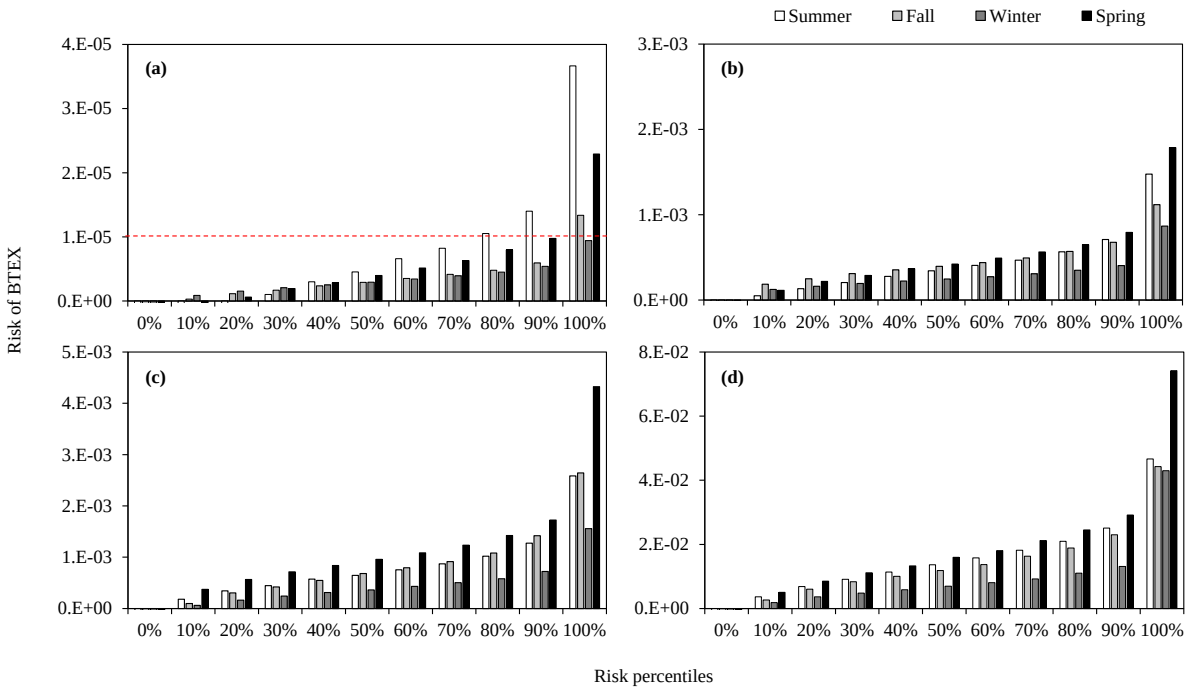

Figure 36. Carcinogenic risk for benzene (a), and non-carcinogenic risk for toluene (b), ethylbenzene (c), and m,p,o-xylenes (d) using Monte Carlo simulation in four seasons.

IV. CONCLUSIONS

In this study, high resolution monitoring of volatile organic compounds using passive air sampler was firstly conducted during four seasons in Ulsan to investigate levels, patterns, spatial distribution, main sources, and risk levels of VOCs in Ulsan.

Concentration of total VOCs were highest in spring, followed by fall, summer, and winter. However, there were no statistically significant differences in sampling periods because Ulsan has significant industrial properties, such as continuously emissions of VOCs from industrial facilities.

As a result of concentration for target compounds, toluene was highest, followed by ethylbenzene, m,p-xylene, o-xylene, and benzene in all sampling periods. In addition, vinyl chloride, which was high in winter, would be effected from landfills and petrochemical facilities, which produce polyvinyl chloride (PVC). Effects from chemical feedstocks and wastewater treatment were explained by 1,3-Butadiene detected at only I3 site during all seasons.

In case of fraction of target groups and BTEX, aromatic groups, which consist of mainly BTEX, accounted for most of VOCs over all sampling periods. Fraction of BTEX at all sampling sites showed a similar pattern, indicating that toluene was highest among BTEX. Exceptionally, fractions of benzene at I3, I4 and I6 sites were higher than toluene in some seasons because vehicular exhausts and non-ferrous facilities would be an influence. Besides, ethylbenzene, m,p-xylene, and o-xylene represented high fractions at I5 and U3 sites, in comparison with emission amounts, these compounds were mostly emitted from shipbuilding and heavy industrial complexes surrounding I5 and I3 sites.

Concentration of total VOCs and BTEX were mainly high at industrial sites and low at urban sites over four seasons, on the other hand, I2 and U2 sites showed quite different patterns. In addition, concentrations of 1,2-dichloroethane and 1,2-dichloropropane at I3 site, and chloroform and cis-1,2-dichloroethylene were at I4 site were relatively higher than other sites. It might probably be due to the effects of similar emission sources.

As a result of spatial distribution, seasonal concentration of total VOCs was high at most of industrial sites in Ulsan, especially at automobile and petrochemical industrial complexes. However, unlike summer and spring, VOCs emitted from industrial facilities seem to go out forward the east sea in fall and winter, therefore, air pollution would be less at urban sites. Despite these reasons, VOC monitoring is required at U2 and U3 sites because these two sites were close to automobile, shipbuilding, and heavy

industrial complexes, and had VOC concentration as high as those in industrial sites. In addition, quite similar patterns with measured concentration and emission amount of BTEX were identified.

Diagnostic ratios (T/B and X/E) showed that Ulsan has significant non-traffic sources such as paints, solvents, and metals except for some sites (traffic effects), moreover, the results also determined that the influence of many kinds from industrial facilities located at various points might be dominant in Ulsan. In addition, Pearson correlation analysis showed strong, good, moderate, and negative correlations with each VOC or CAP. Through these results, the relationships were expected such as compounds emitted from the same surrounding industrial complexes or sites, for instance, ethylbenzene and m,p-xylene were detected and emitted from shipbuilding and heavy industrial complexes.

As a result of risk assessment using Monte Carlo simulation, risk of benzene in the worst case was higher than acceptable levels at 1.E-06 (US EPA) and 1.E-05 (WHO). It can expect that carcinogenic risk of benzene may reach high levels in case of hazardous chemical accidents. On the other hand, risks of toluene, ethylbenzene, m,p,o-xylene did not exceed the standard acceptable HQ (US EPA) despite high concentration in this study.

In conclusion, seasonal monitoring of VOCs should be continuously conducted in Ulsan. Furthermore, passive and active air samplers should be used because understanding variations by time scare, spatial and temporal distribution of VOCs are important. Also, positive matrix factorization (PMF) or air dispersion models should be used to identify the main sources of VOCs in details. In addition, in case of risk assessment of VOCs, exceeding or non-exceeding acceptable levels is not important, therefore, risks of various VOCs which have cancer risk should also be assessed and required in further study.

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SUPPLEMENTARY

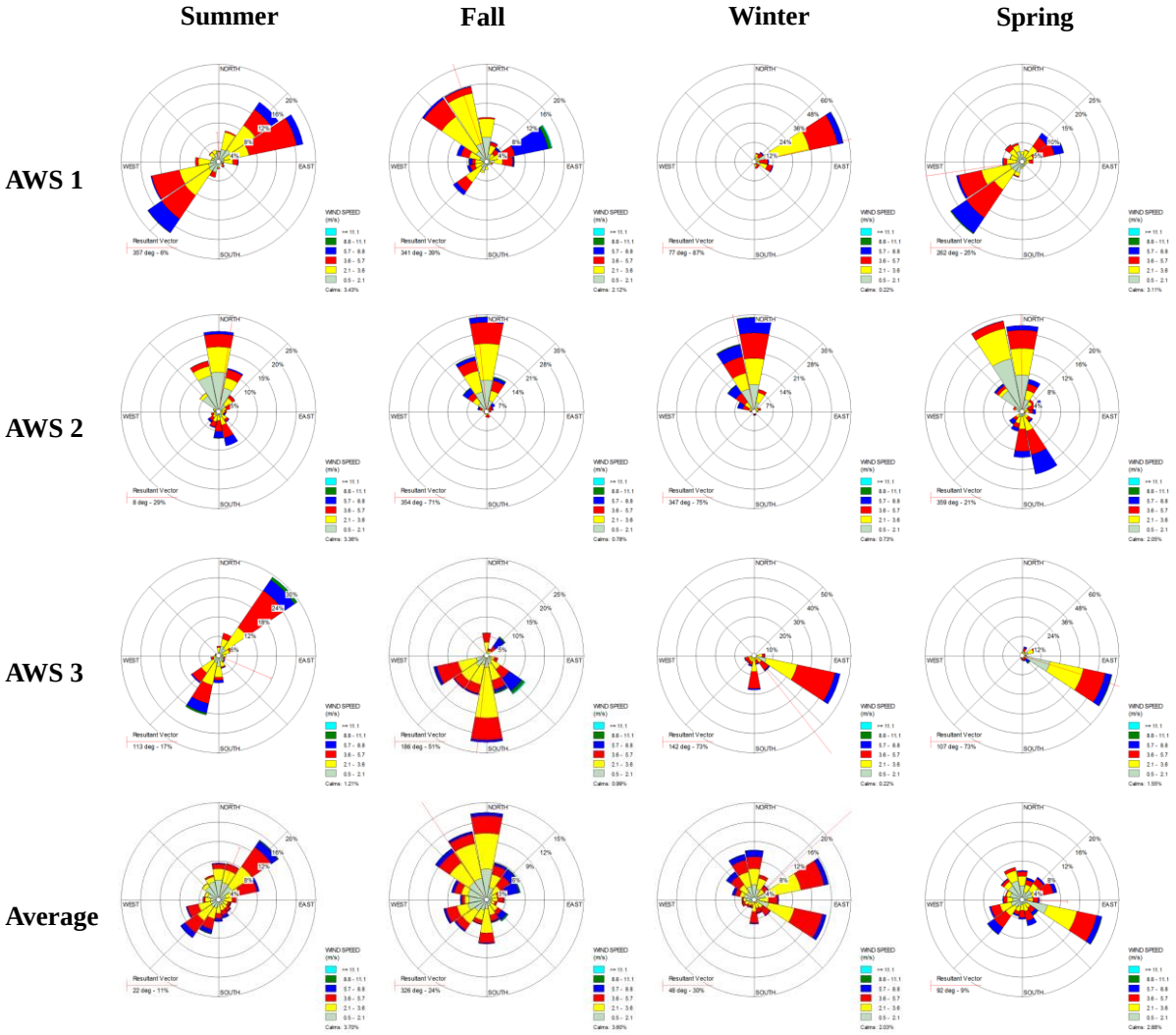

Figure S1. Seasonal wind rose at AWS1, AWS2, and AWS3 and average wind rose investigated in this study.

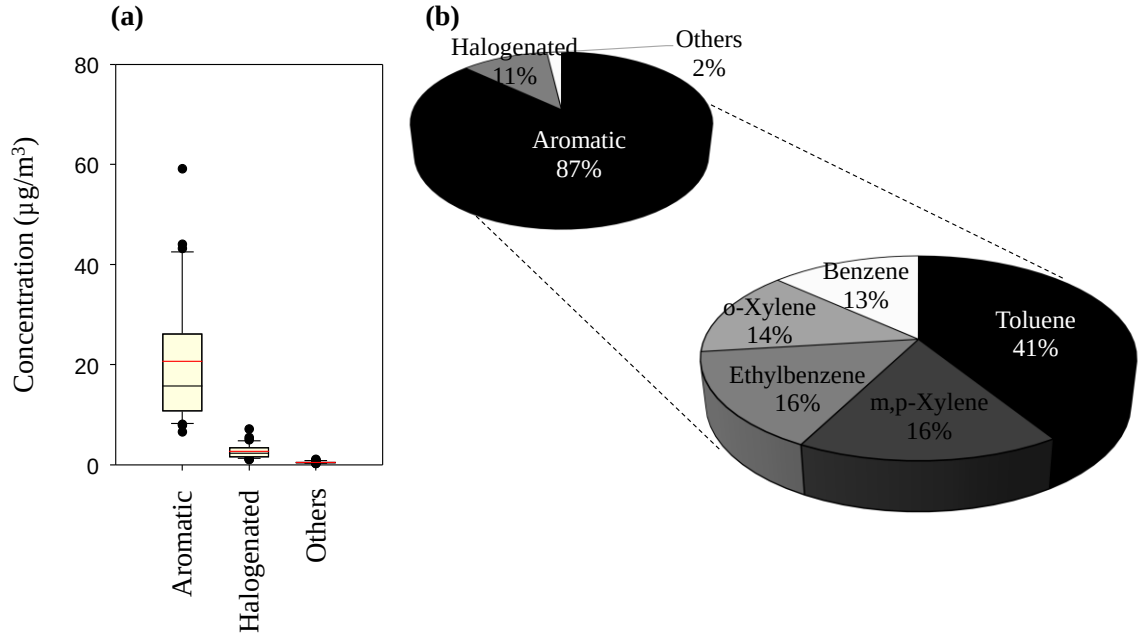

Figure S2. The concentration of three groups (a) and fraction of detailed aromatic group based on the summer levels (b).

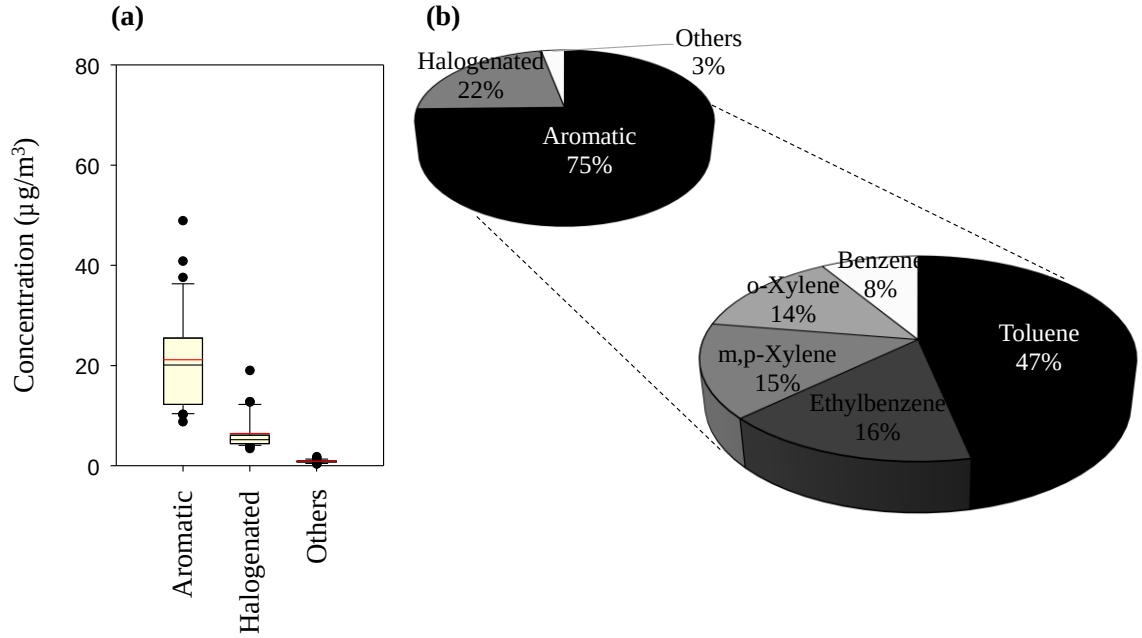

Figure S3. The concentration of three groups (a) and fraction of detailed aromatic group based on the fall levels (b).

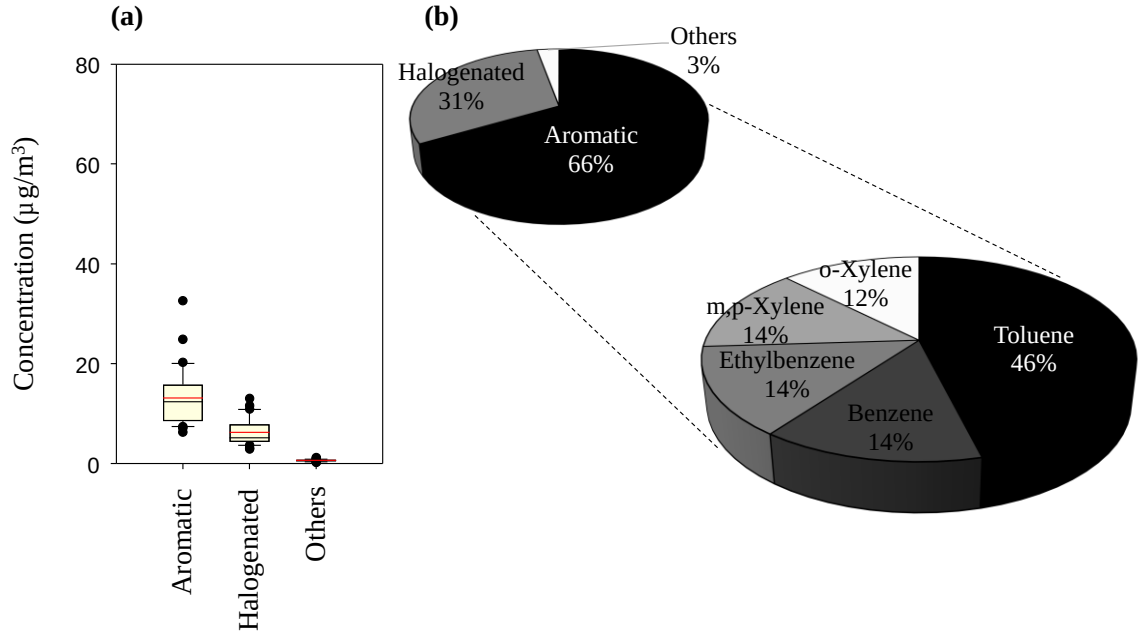

Figure S4. The concentration of three groups (a) and fraction of detailed aromatic group based on the winter levels (b).

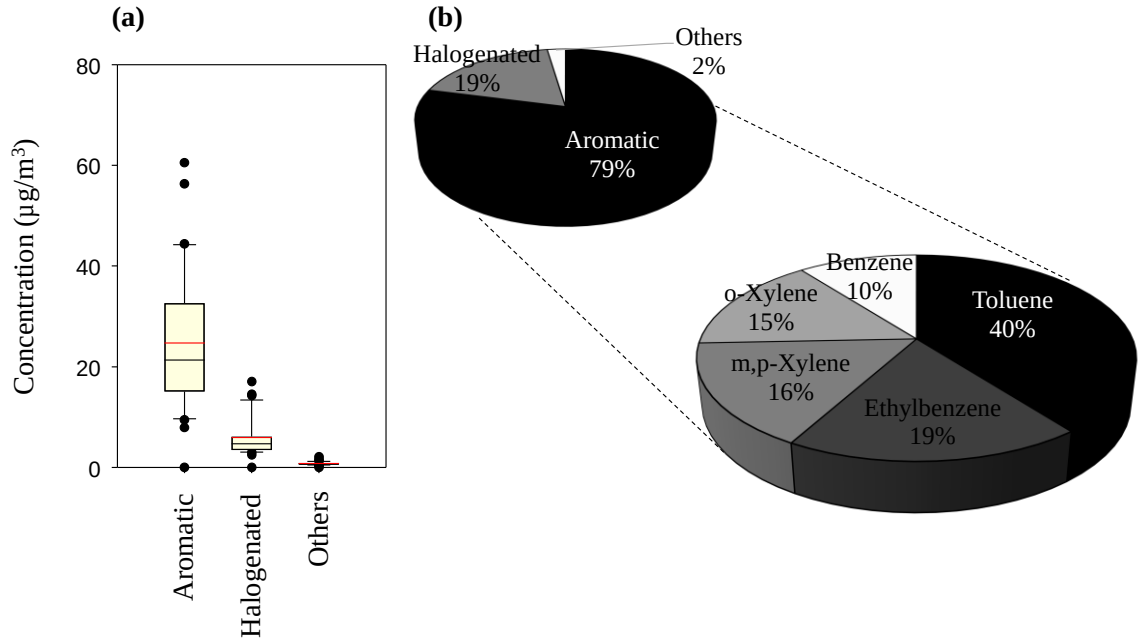

Figure S5. The concentration of three groups (a) and fraction of detailed aromatic group based on the spring levels (b).

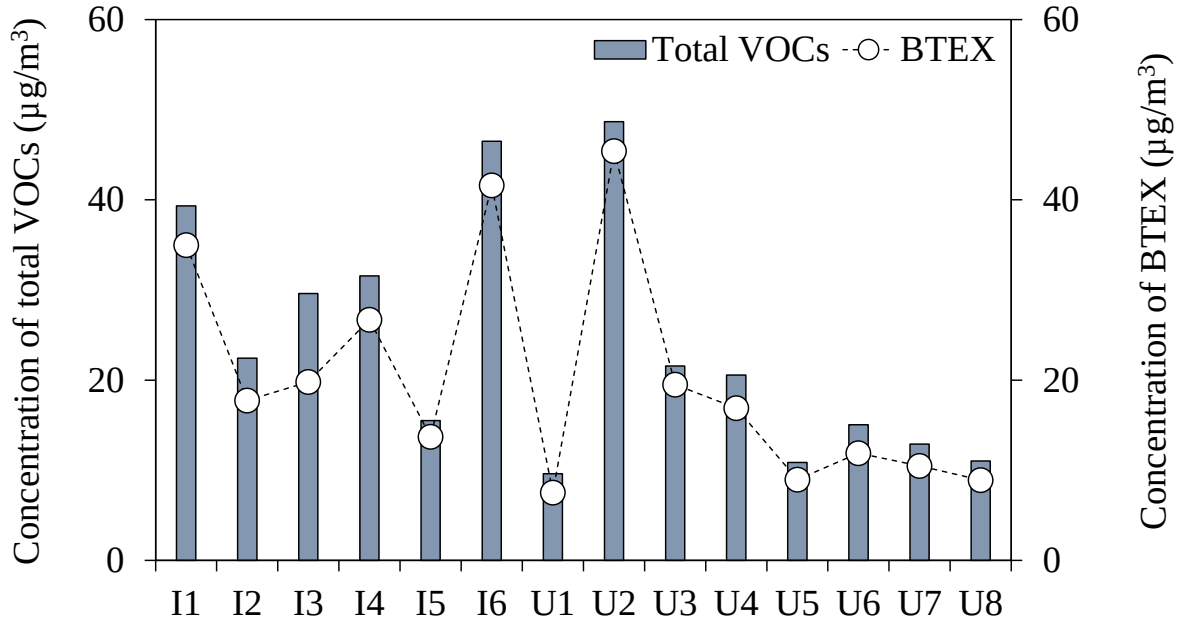

Figure S6. Concentration of total VOCs and BTEX at each sampling site in summer.

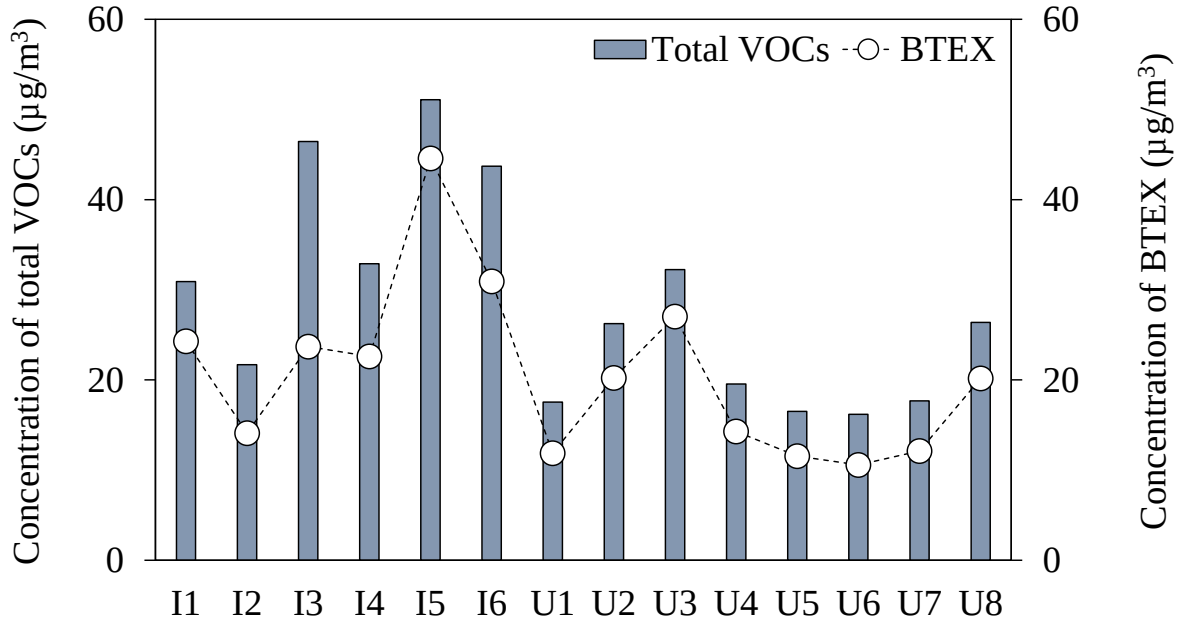

Figure S7. Concentration of total VOCs and BTEX at each sampling site in fall.

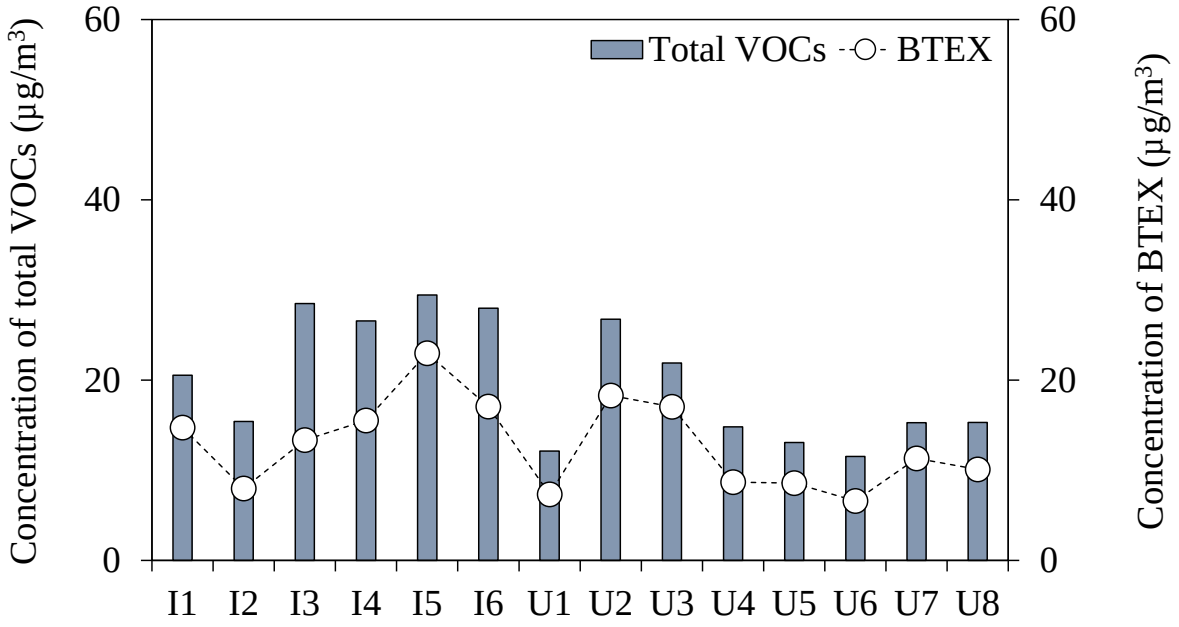

Figure S8. Concentration of total VOCs and BTEX at each sampling site in winter.

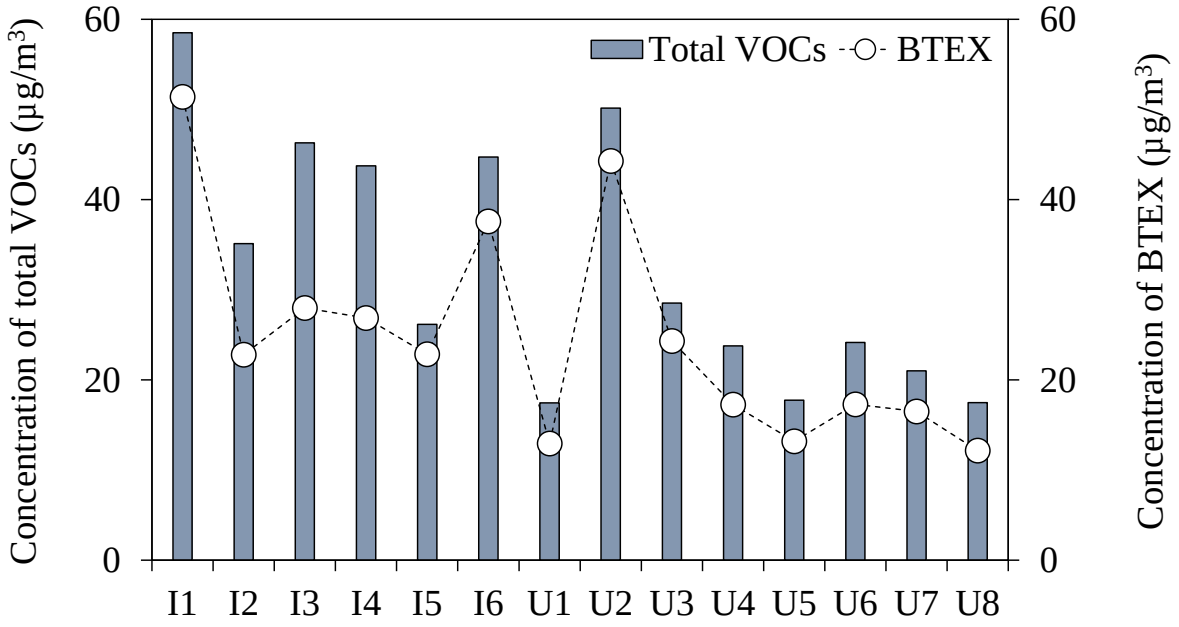

Figure S9. Concentration of total VOCs and BTEX at each sampling site in spring.

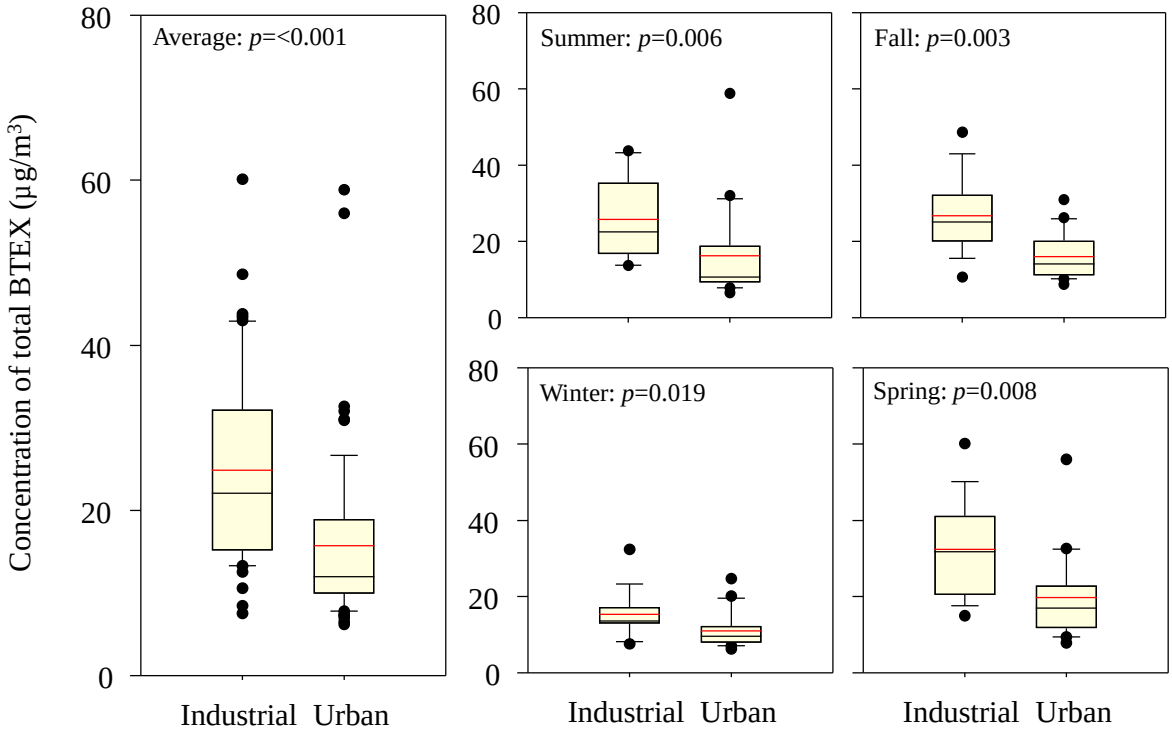

Figure S10. Comparison with concentration of BTEX at industrial and urban site in annual average, summer, fall, winter, and spring.

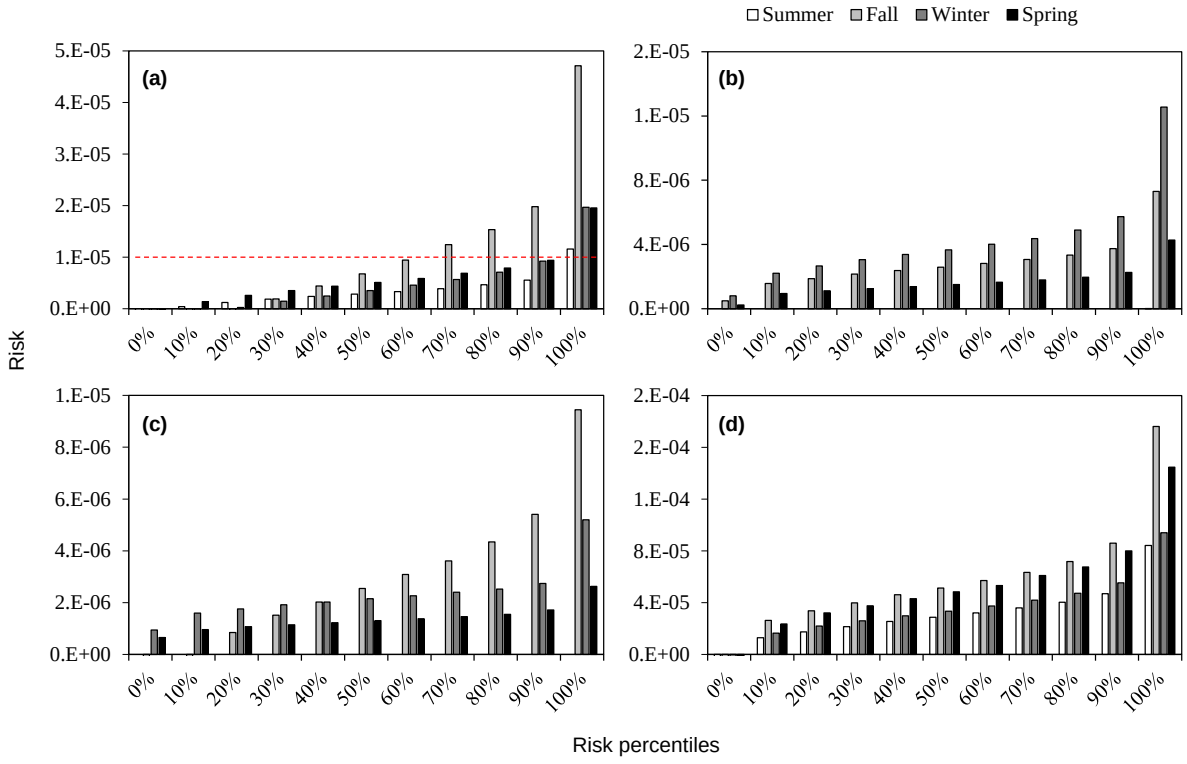

Figure S11. Carcinogenic risk for 1,2-dichloroethane (a), vinyl chloride (b), 1,3-butadiene (c), and non-carcinogenic risk for MTBE (d) using Monte Carlo simulation in four seasons.

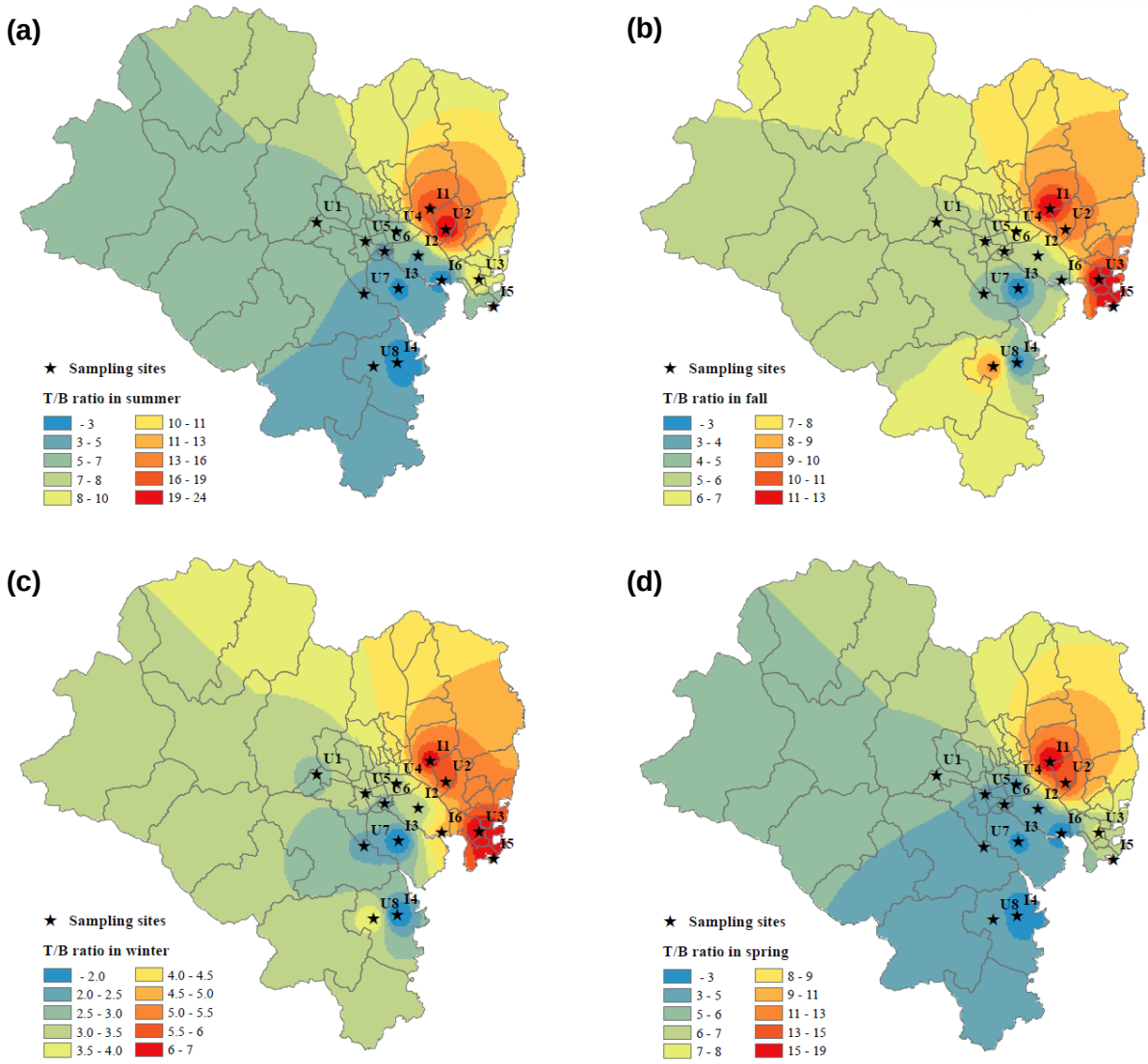

Figure S12. Spatial distribution of toluene/benzene (T/B) ratio at sampling sites in summer (a), fall (b), winter (c), and spring (d).

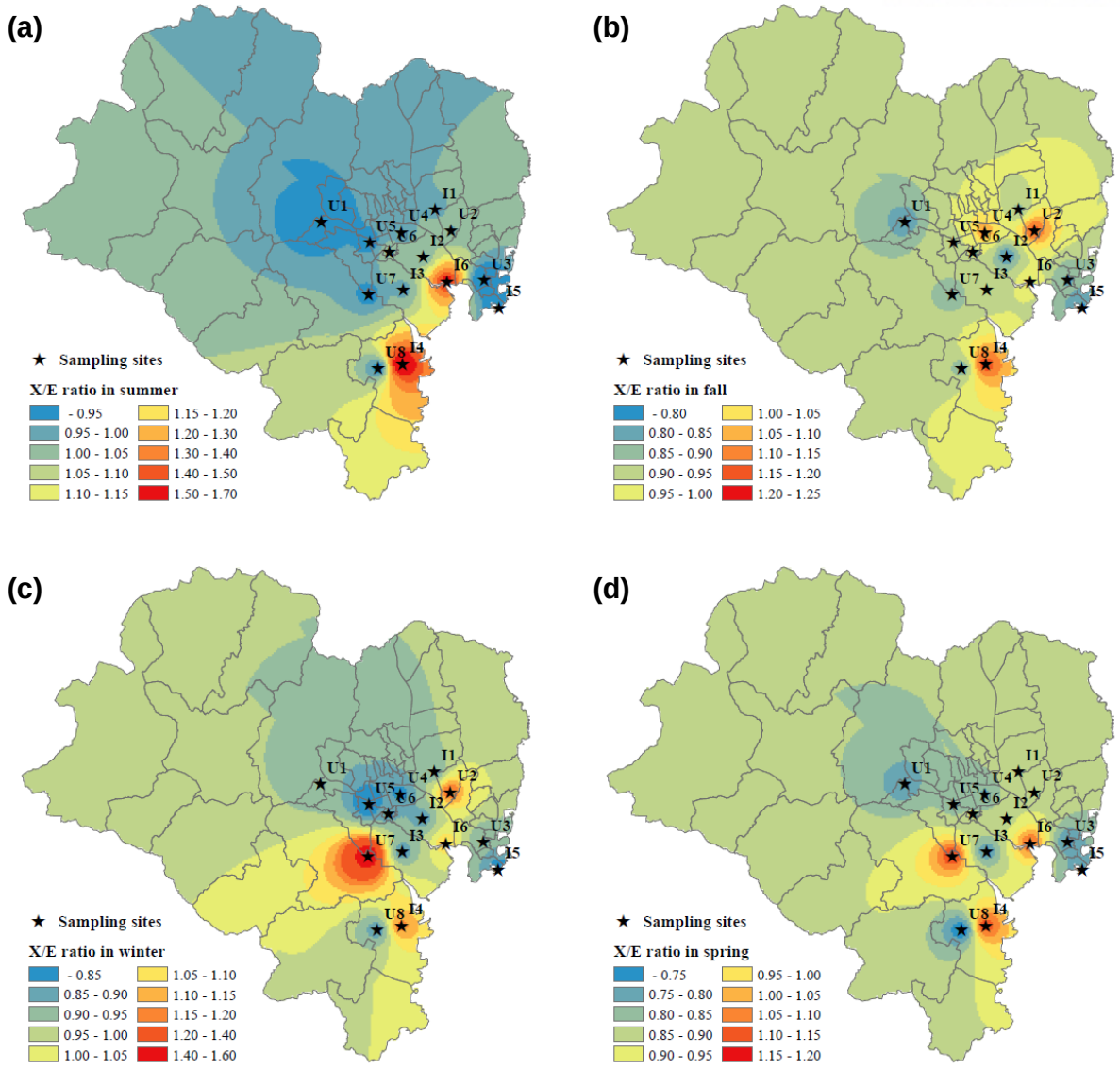

Figure S13. Spatial distribution of m,p-xylene/ethylbenzene (X/E) ratio at sampling sites in summer (a), fall (b), winter (c), and spring (d).

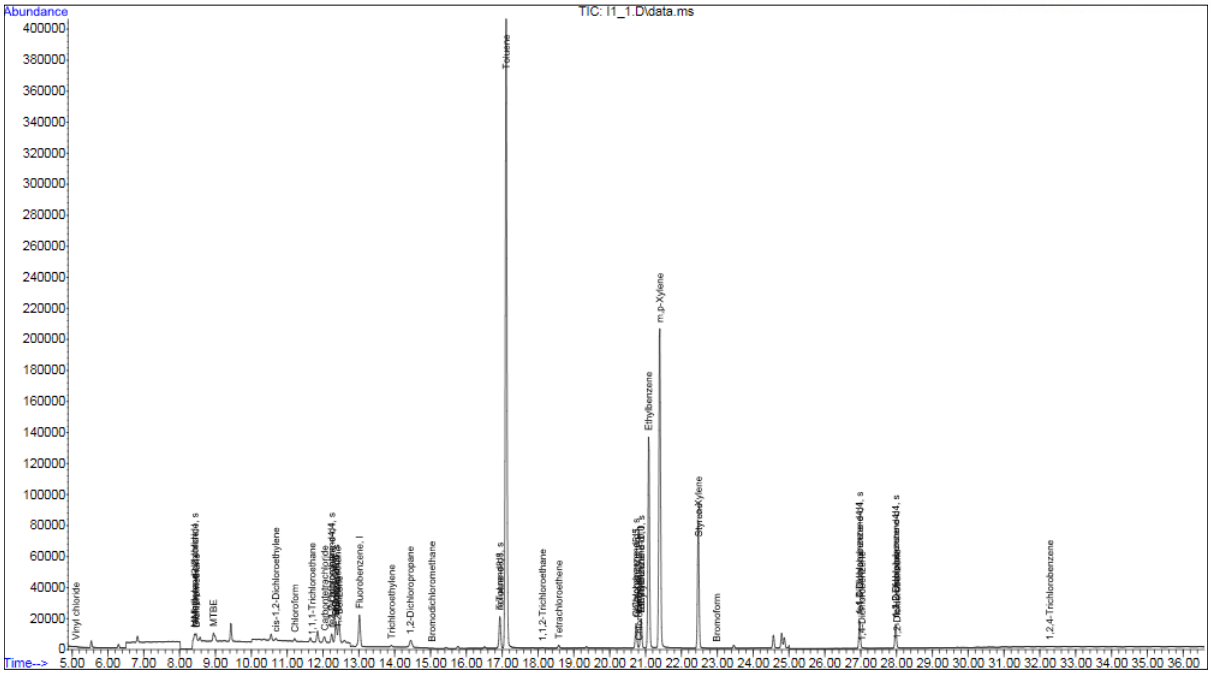

Figure S14. Chromatogram of real sample at industrial site (VOCs).

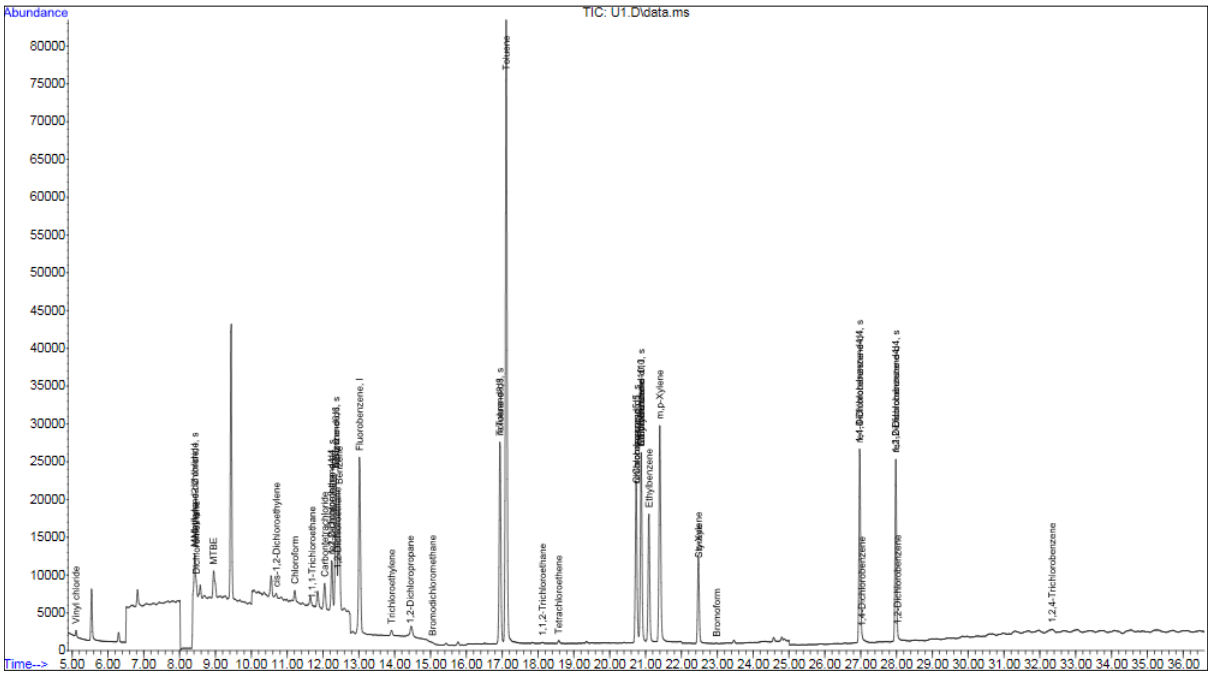

Figure S15. Chromatogram of real sample at urban site (VOCs).